

# Chemicals used for treatment of water intended for human consumption — Ozone

ICS 13.060.20; 71.100.80

## National foreword

This British Standard is the UK implementation of EN 1278:2010. It supersedes BS EN 1278:1999 which is withdrawn.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.

This publication does not purport to include all the necessary provisions of a contract. Users are responsible for its correct application.

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English Version

**Chemicals used for treatment of water intended for human  
consumption - Ozone**

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

Produkte zur Aufbereitung von Wasser für den  
menschlichen Gebrauch - Ozon

This European Standard was approved by CEN on 28 February 2010.

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## Foreword

This document (EN 1278:2010) 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of an identical text or by endorsement, at the latest by October 2010, and conflicting national standards shall be withdrawn at the latest by October 2010.

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 1278:1998.

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, 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.

Differences between this edition and EN 1278:1998 are editorial to harmonize the text with other standards in this series.

## Introduction

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

- 1) this 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 the 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 ozone used for treatment of water intended for human consumption. It describes the characteristics of ozone and specifies a test method for determining the ozone concentration in other gases.

## 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, *Water for analytical laboratory use — Specification and test method (ISO 3696:1987)*

## 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<sub>3</sub>

#### 3.1.5

##### chemical formula

O<sub>3</sub>

#### 3.1.6

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

10028-15-6

#### 3.1.7

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

Not applicable

### 3.2 Commercial form

Ozone is generated on or near the site of use.

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1) Chemical Abstracts Service Registry Number

2) European Inventory of Existing Commercial Chemical Substances

### 3.3 Physical properties

#### 3.3.1 Appearance

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<sup>3</sup> at NTP (Normal Temperature Pressure, 273 K and 101,3 kPa);

Liquid : 1,574 g/cm<sup>3</sup> at - 183 °C;

Solid : 1,728 g/cm<sup>3</sup>.

#### 3.3.3 The gas-liquid partition coefficient

In pure water, the partition coefficient 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 — The gas-liquid partition coefficient between water and gas phase**

Temperature of water  °C	Solubility  S, in $\frac{\text{g/m}^3 \text{H}_2\text{O}}{\text{g/m}^3 \text{gas}}$
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	0,0147
- 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 <sup>3)</sup>**

- 112 °C.

NOTE : Vaporization heat : 681 kJ/m<sup>3</sup>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;

0,0015 5 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) 100 kPa = 1 bar

### 3.4 Chemical properties

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

( $E_o^H$  -values in volts):



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:

$$\text{O}_3 (1) = 1,66 \text{ V};$$

$$\text{O}_3 (2) = 0,82 \text{ V};$$

$$\text{OH}^\circ (3) = 2,21 \text{ V}.$$

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  $\text{OH}^\circ$  : ( $\text{O}_3 + \text{H}_2\text{O} \rightarrow 2 \text{OH}^\circ + \text{O}_2$ ). The  $\text{OH}^\circ$  radical is a strong general oxidant.

## 4 Purity criteria

### 4.1 General

This European Standard specifies the minimum purity requirements for Ozone 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 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 lead to significant quantities of impurities, by-products or additives being present, this shall be notified to the user.

### 4.2 Composition of commercial product

Ozone is obtainable in air, oxygen or air enriched in oxygen.

Typical concentrations obtainable in air are in the range of 15 g/m<sup>3</sup> to 45 g/m<sup>3</sup> (NTP) and, in oxygen 40 g/m<sup>3</sup> to 200 g/m<sup>3</sup>(NTP).

The concentration (in grams per cubic metre NTP) at the nominal operating condition of the generators shall be specified in the tendering documents.

### 4.3 Impurities and main by-products

See A.3.2.

## 4.4 Chemical parameters

NOTE For the purpose of this standard "chemical parameters" are those defined in the 98/83/EC: Council Directive of 3 November 1998 on the quality of water intended for human consumption. (see [1]).

None of the chemical parameters according to the directive 98/83/EC are found in the gaseous ozone phase. Pesticides and polycyclic aromatic hydrocarbons are not by-products of the ozone manufacturing processes.

## 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 metre, 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 (see table A.1) or in polyfluorocarbene material resistant to ozone. The transfer of the gas from the sampling point to the analyzer shall be kept shorter than 1 min.

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

NOTE 1  $1 \text{ g/m}^3$  (NTP) equals  $466,4 \times 10^{-6}$  (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  $20 \text{ g/m}^3$  (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  $1 \text{ g/m}^3$  to  $200 \text{ g/m}^3$  (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 phosphite ( $\text{Na}_2\text{HPO}_4 \cdot 2 \text{H}_2\text{O}$ ) solution at 7,3 g/l and potassium dihydrogen phosphate ( $\text{KH}_2\text{PO}_4$ ) solution at 3,5 g/l.

**5.2.3.2** Sodium thiosulfate : standard volumetric, solution  $c(\text{Na}_2\text{S}_2\text{O}_3) = 0,1 \text{ mol/l}$ .

**5.2.3.3** Sulfuric acid, solution at 9 mol/l.

**5.2.3.4** Potassium iodate (KIO<sub>3</sub>) powdered.

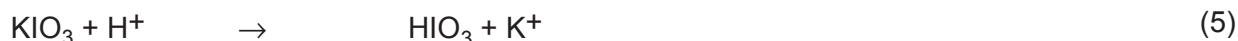
**5.2.3.5** Potassium iodide (KI) crystalline.

**5.2.3.6** Hydrochloric acid standard volumetric solution  $c(\text{HCl}) = 0,1 \text{ mol/l}$  or sulfuric acid  $c(\text{H}_2\text{SO}_4) = 0,05 \text{ mol/l}$ .

**5.2.3.7** Zinc iodide (ZnI<sub>2</sub>)-starch indicator. Disperse 4 g starch into a small quantity of water. Add the dispersion to a solution of 20 g zinc chloride (ZnCl<sub>2</sub>) 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<sub>2</sub>.

**5.2.3.8** Standardization of sodium thiosulfate:

#### **5.2.3.8.1 Reactions**



#### **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:

$$c_t = \frac{c_a \times V}{V_t} \quad (8)$$

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<sup>3</sup> to 200 g/m<sup>3</sup> (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 equation:

$$C = \frac{V \times c_t \times 24}{v} \quad (9)$$

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<sup>3</sup> (NTP), the standard deviation is 0,03 g/m<sup>3</sup> (NTP), for ozone produced from air at a nominal concentration of 20 g/m<sup>3</sup> (NTP). For higher concentrated ozone gases (range of 100 g/m<sup>3</sup> to 200 g/m<sup>3</sup> (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 metre or bubble trap is recommended).

# 6 Labelling - Transportation – Storage

## 6.1 Means of delivery

For local brief duration buffer storage 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, 16 bar standard) can be convenient if the content in plasticizer is low but some formulations can be subject to ageing when exposed to ozone at high concentrations. Rubber and plastic materials e.g. for joints shall be proven specifically for resistance to ozone.

## 6.2 Risk and safety labelling according to the EU Directives<sup>4)</sup>

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.

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

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 Stability

6.5.1 Temperature can influence the decomposition rate (see [8]).

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

6.5.3 In a dry process gas at 100 kPa and 298 K, the half-life time of ozone is higher than 2 h .

6.5.4 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. Presence of reactive organic substances can promote the ozone decomposition by reaction. In such cases the reactions are generally of second order.

6.5.5 Decomposition is accelerated in alkaline solution. A typical value of the pseudo first order overall kinetic constant is

$$k_1 = 2 \times 10^{-2} \cdot s^{-1} \text{ (at pH = 10 and an alkalinity in the range of } 10^{-2} \text{ mol/l to } 10^{-4} \text{ mol/l).}$$

6.5.6 Decomposition of ozone also occurs through synergetic processes (the so-called Advanced Oxidation Processes) "AOP's", involving ozone together with hydrogen peroxide, UV-radiation or catalysts.

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4) See [9].

## Annex A (informative)

### General information on ozone

#### A.1 Origin

##### A.1.1 Raw materials

Ozone is currently obtained by processes involving the dissociation of molecular oxygen contained in air, oxygen or air-oxygen mixtures, into oxygen radicals which can react with molecular oxygen to form ozone.

Hydrocarbons should be minimized in the process gas. At 1 % volume fraction of hydrocarbons in air, practically no ozone is generated anymore, and, the drop in yield is linear in function of the hydrocarbon content of the process gas.

In the process gas, the recommended limit for content of hydrocarbons (expressed as methane), is  $15 \times 10^{-6}$  (volume fraction). This point should be checked occasionally when cryogenic oxygen is used and generated in areas with industrial pollution of the ambient air (Optional analytical method, see A.3.3 ; Methane index).

##### A.1.2 Manufacturing process

At present, 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 process gas (dew point below - 50 °C).

In air,  $1 \text{ g/m}^3$  (NTP) corresponds to  $0,020 \text{ 8 mol/m}^3$  or to a mass fraction of 0,077 3 % ; in oxygen,  $1 \text{ g/m}^3$  (NTP) corresponds also to  $0,020 \text{ 8 mol/m}^3$  or to a mass fraction of 0,069 9 %.

##### A.1.3 Materials suitable for contact with ozone

Use of high grade (molybdenum) steel is recommended in view of corrosion resistance (see table A.1).

At the time of publication of the present standard, no European document dealing with this topic exists.

Table A.1 shows, for information, a comparison between hues (considered as equivalent) of stainless steels defined by the standard in Belgium, France, Germany, Sweden and United Kingdom in order to help users with equivalency problems.

However, this information is only general because many other factors interfere : conditions of use, thermal treatment, nature and sizes of the product. Therefore the user should contact competent organizations for further information.

**Table A.1 — Correspondence of stainless steel codes applicable to ozone equipments (1996)**

Belgium	France	Germany	Sweden	U K
316	Z6 CND 17.11	1.4401	2347	316 S 31
316	Z6 CND 17.12	1.4436	2343	316 S 33
316 L	Z2 CND 17.12	1.4404	2348	316 S 13
316 L	Z2 CND 17.13	1.4435	2353	316 S 13
316 Ti	Z6 CND 17.12	1.4571	2350	320 S 31

## A.2 Use

### A.2.1 Function

Ozone is applicable in water treatment for disinfection, improvement of general organoleptic quality of water, removal of iron and manganese, colour removal, advanced oxidation of persistent pollutants and as a reagent promoting coagulation.

### 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 a process gas.

### A.2.3 Treatment dose

Treatment dose with ozone is variable in function of the water quality and the object of the treatment.

General guidelines are:

- a) for disinfection, including inactivation of viruses and parasites; a dose is applied to obtain a residual concentration of 0,4 mg/l after 4 min to 6 min contact time. This also meets the general acceptance parameters such as color, taste and odour. In finished waters the required dose is usually in the range of 2 mg/l to 4 mg/l;
- b) for initiating biological treatment, a preliminary rule-of-thumb is to consider a dose of 0,2 mg to 0,3 mg ozone per milligram of total organic carbon;
- c) for oxidation of iron and manganese, the required dose can be determined from the stoichiometry of the reactions together with the ozone consumption due to other components of the water;
- d) for assisting coagulation the required dose generally does not exceed 1 mg/l and over-treatment should be avoided.

In all instances it is recommended to make a preliminary evaluation by a laboratory investigation and, if possible a pilot trial.

### 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 techniques presently used for the treatment of drinking water are porous diffusers, injectors, dispersing turbines and packet towers.



## A.2.5 Secondary effects

Ozone can form oxidation by-products. The reaction products are more readily assimilable and thus stimulate biological growth. In certain conditions, limited formation of brominated trihalomethanes and of bromate can occur on ozonation of bromide containing waters (further information, see references in [2], [3] and [4]).

## A.2.6 Removal of excess product

Ozone self-decomposes in water. Normally no process for removal at practical dosing rates is required. When consumed immediately after treatment, ozonated water is best aerated for example by cascades or other degassing processes of the residual concentration. Removal of residual ozone in water is also achieved by filtration on granular active carbon.

Excess ozone in the off-gas should be kept under appropriate control. Presently available technics are thermal or catalytic decomposition and adsorption with or without reduction. Technologies based on the use of sulfur dioxide (SO<sub>2</sub>) are also applicable.

## A.3 Operational control methods

### A.3.1 Ozone concentration measurement in a process gas by UV absorption

#### A.3.1.1 General

The present method concerns the determination of ozone in air, oxygen or other process gases. The ozone concentration range is of 1 g/m<sup>3</sup> to 200 g/m<sup>3</sup> (NTP).

#### A.3.1.2 Principle

The strong absorbance by ozone of wavelengths between 200 nm and 300 nm (Hartley band) is used for the determination of ozone concentration in the gas phase. The method is instrument-dependent but based on the Beer-Lambert absorption law. The molar absorbance coefficient (base log 10), of ozone at 253,7 nm ( the wavelength of low pressure Hg-lamps) is

$$\varepsilon = 3\,000 \text{ cm}^{-1} \text{ mol}^{-1} \text{ l with an uncertainty of 1 \%.$$

The absorbance can also be expressed in the form of the molar absorbance cross section (base 10), of  $s_{M,10} = 300 \text{ m}^2/\text{mol}$ .

#### A.3.1.3 Influence of temperature and pressure

To be expressed at Normal Temperature (T<sub>N</sub>) and Pressure (P<sub>N</sub>) (i.e. 273 K and 101,3 kPa), the concentration, as measured should be corrected :

$$C(\text{NTP}) = C(\text{measure}) \times \frac{T(\text{measure})}{P(\text{measure})} \times \frac{P_N}{T_N} \quad (10)$$

#### A.3.1.4 Accuracy

With good instrumentation a relative accuracy of 2 % can be attained. The method should be best calibrated with the iodometric method described in 5.2. The relative accuracy can also be checked with calibrated quartz filters having an optical density (base 10) of 0,5 to 1,0 at 253,7 nm.

### A.3.1.5 Precautions

**A.3.1.5.1** Only ozone-resistant materials should be used for the gas transfer lines.

**A.3.1.5.2** Particular care should be taken to avoid leakages in the gas transfer lines.

**A.3.1.5.3** The path-length of the optical cells should be appropriate to measure an optical density between 0,5 and 1,0 with the expected ozone concentration.

**A.3.1.5.4** Double beam instruments are preferable. If single path instruments are used an incorporated internal standard for checking of the light transmission ranges should be installed.

**A.3.1.5.5** To avoid ozone destruction, a minimum gas flow of 1 l/min should transit through the optical cell.

### A.3.1.6 Further information

See [2].

## A.3.2 Detection of nitrogen oxides : $N_2O_5$ Index

### A.3.2.1 General

Traces of nitrogen oxides can be formed in the generation of ozone by high-potential electrical discharge through a nitrogen-containing process gas like air. This occurs by dissociation of nitrogen into atoms-radicals which combine with the oxygen radicals formed in the discharge. Different nitrogen oxides can be formed transiently but by a series of equilibrating reactions the end products are :  $N_2O_5 \rightarrow 2 NO_2 + \frac{1}{2} O_2$ , which is the stable term in presence of an excess of ozone. Traces of gaseous nitric acid can be formed also by reaction of  $N_2O_5$  with water vapour when present in the process gas.

In good practice, the amount of nitrogen oxides, including nitric acid, expressed as  $N_2O_5$  is less than 5 g/kg ozone. Because this amount is not relevant in drinking water treatment, the analytical control of nitrogen oxides in ozone process gases is not a necessary routine procedure. The formation of nitrogen oxides can become more significant in case of inadequate air drying promoting the occurrence of spark-discharges in the ozone generator or, through an overload in electrons vs. the oxygen concentration in the discharge. This situation can occur when the gas flow is set much lower than the design value. In such cases, and also for fundamental studies, the determination of the nitrogen oxide-index can be required.

### A.3.2.2 Principle

Most nitrogen oxides have significant absorption bands in the IR-range but most of them do not coexist with ozone.

**NO :** 5,33  $\mu m$  ( $= 1\ 876\ cm^{-1}$ ) ; very weak in  $O_3$ /air.

**NO<sub>2</sub> :** 6,18  $\mu m$  ( $= 1\ 618\ cm^{-1}$ ) ; very weak in  $O_3$ /air.

**HNO<sub>3</sub> (gas) :** 5,86  $\mu m$  ( $= 1\ 706\ cm^{-1}$ ) corresponds to NO-stretching.

7,51  $\mu m$  ( $= 1\ 332\ cm^{-1}$ ) corresponds to NO-deformation.

7,55  $\mu m$  ( $= 1\ 325\ cm^{-1}$ ) corresponds to NO-deformation.

**N<sub>2</sub>O<sub>5</sub> :** 5,79  $\mu m$  ( $= 1\ 727\ cm^{-1}$ ) corresponds to (overlapping) anti symmetrical stretching.

8,02  $\mu\text{m}$  ( $= 1\,247\text{ cm}^{-1}$ ) corresponds to symmetrical stretching.

**N<sub>2</sub>O :** 4,5  $\mu\text{m}$  ( $= 2\,222\text{ cm}^{-1}$ ) (does not exist in O<sub>3</sub>/air).

**OZONE :** 4,8  $\mu\text{m}$  ( $= 2\,083\text{ cm}^{-1}$ ) ; 9,48  $\mu\text{m}$  to 9,6  $\mu\text{m}$   
 ( $= 1\,055\text{ cm}^{-1}$  to  $1\,042\text{ cm}^{-1}$ ) corresponds to valence deformation bands.

The selected wavelength for the determination of N<sub>2</sub>O<sub>5</sub>-Index is 8,02  $\mu\text{m}$  or  $1\,247\text{ cm}^{-1}$ .

### **A.3.2.3 Method**

#### **A.3.2.3.1 Apparatus**

Double beam IR-spectrometer equipped with a flow-through gas cell of minimum path length of 10 cm or with a multiple reflection gas cell.

#### **A.3.2.3.2 Calibration gases**

Oxygen; purity higher than 99,998 % volume fraction.

Nitrogen including up to 10 % volume fraction of argon : purity (nitrogen + argon) higher than 99,999 5 % volume fraction.

Synthetic air obtained by mixing 20 % of oxygen with 80 % of nitrogen ; N<sub>2</sub>O<sub>5</sub>-NO<sub>2</sub> synthetic as 1,85 g/m<sup>3</sup> (NTP), in synthetic air.

#### **A.3.2.4 Accuracy**

Detection limit is 0,2 g/m<sup>3</sup> (NTP) expressed as N<sub>2</sub>O<sub>5</sub> ; the standard deviation is 0,1 g/m<sup>3</sup> expressed as N<sub>2</sub>O<sub>5</sub> (NTP).

#### **A.3.2.5 Further information**

See [6]. and [7].

### **A.3.3 Analytical control of hydrocarbon content in an ozonation process gas. Methane index**

#### **A.3.3.1 General**

Traces of hydrocarbons can exist in the process gases submitted to the electrical discharge for ozone generation. Their origin is environmental air pollution but, also from leachates of materials in contact with the gas, improper functioning of lubricated air compressors, etc.

The hydrocarbons in the process gas are important since they can drop the generation yield. The issue is of greater importance when using oxygen for the generation of high ozone concentrations. In that case the recommended limit concentration is set at  $15 \times 10^{-6}$  volume fraction expressed as "methane index". The determination of the hydrocarbon content in the process gas is not a routine analysis in the ozonation practice of drinking water. The present recommended method is intended for occasional control, fundamental developments and general information.

### A.3.3.2 Principle

Determination of hydrocarbons by flame-ionization detection.

The method can be applied on discrete samples or also as a continuous monitoring technique with both fixed or portable equipment. The exact experimental conditions of the technique are instrument-dependent.

**A.3.3.3** The general principle is to feed a sample through a hydrogen-helium (40/60) fuel and air burner placed in an ionization detector. With hydrogen alone a negligible number of ions is produced, however, when hydrocarbons are present in the sample, ions are produced. Due to the electrostatic field produced between the burner and the collector on applying a polarizing voltage, (usually the burner is negative and collector is positive), an ionization current is obtained which, for low concentrations, is directly proportional to the hydrocarbon concentration in the flame-gases.

### A.3.3.4 Calibration

The system should be calibrated with methane-air or methane-oxygen mixtures. "Zero-grade" calibration and feed gases are required.

### A.3.3.5 Accuracy

The currently achieved detection limit is  $0,05 \times 10^{-6}$  volume fraction with a standard deviation of less than  $0,02 \times 10^{-6}$  volume fraction. Instrumental drift should be checked and, is usually less than  $0,04 \times 10^{-6}$  volume fraction in 24 h. The response time level should be fixed at 95 % of full scale in 1 s. Standard measuring ranges are  $0 \times 10^{-6}$  volume fraction to  $40 \times 10^{-6}$  volume fraction.

## Annex B (normative)

### General rules relating to safety

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

Ozone is toxic by inhalation. The threshold limit value is defined as the maximum acceptable time-weighted average concentration in working rooms for 8 h a day exposure. The commonly adopted value is presently set at  $0,1 \times 10^{-6}$  volume fraction. Monitoring in ambient air shall be required. Ozonation premises potentially exposed to ozone leakage shall be naturally vented and forced venting equipment to be operated in case of leakages of the hardware (see also [3]).

Risks of fire for the present operational ozone generating systems are the same for those of leakage in oxygen systems.

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

Explosion risks exist on liquefying and evaporation of ozone containing mixtures.

#### 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 exposure, practise artificial respiration, and call for medical assistance.

##### B.2.2 Spillage

In case of leakages, stop the generators and vent the premises. In permanent operation residual ozone destruction in the off-gas is recommended (see [2], [3] and [4]).

##### B.2.3 Fire

No specific fire hazard is related to ozone at the presently generated ozone concentrations (see 4.2). Instructions concern the use of process gases rich in oxygen. For electrical risks, standards and codes of practice shall be applied.

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