BRITISH STANDARD

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BS 6068-2.32:
1995

Water quality —

Determination of permanganate index

Confirmed
July 2008

The European Standard EN ISO 8467:1995 has the status of a British Standard

Cooperating organizations

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Contents

National foreword

This British Standard has been prepared under the direction of the Environment and Pollution Standards Policy Committee and is the English language version of EN ISO 8467:1995 *Water quality — Determination of permanganate index* published by the European Committee for Standardization (CEN). It is identical with ISO 8467:1993, published by the International Organization for Standardization (ISO). This standard supersedes BS 6068-2.32:1987, which is withdrawn.

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Summary of pages

This document comprises a front cover, an inside front cover, pages i and ii, the EN ISO title page, pages 2 to 6, an inside back cover and a back cover.

This standard has been updated (see copyright date) and may have had amendments incorporated. This will be indicated in the amendment table on the inside front cover.

EUROPEAN STANDARD
NORME EUROPÉENNE
EUROPÄISCHE NORM

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Descriptors: Water, quality, water tests, chemical analysis, determination, permanganate number

English version

Water quality — Determination of permanganate index

(ISO 8467:1993)

Qualité de l'eau — Détermination de l'indice de permanganate
(ISO 8467:1993)

Wasserbeschaffenheit — Bestimmung des Permanganat-Index
(ISO 8467:1993)

This European Standard was approved by CEN on 1994-11-03. CEN members are bound to comply with the CEN/CENELEC Internal Regulations which stipulate the conditions for giving this European Standard the status of a national standard without any alteration.

Up-to-date lists and bibliographical references concerning such national standards may be obtained on application to the Central Secretariat or to any CEN member.

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CEN

European Committee for Standardization
Comité Européen de Normalisation
Europäisches Komitee für Normung

Central Secretariat: rue de Stassart 36, B-1050 Brussels

Ref. No. EN ISO 8467:1995 E

Foreword

This European Standard has been taken over by the Technical Committee CEN/TC 230, Water analysis, from the work of ISO/TC 147, Water quality, of the International Organization for Standardization (ISO).

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 September 1995 and conflicting national standards shall be withdrawn at the latest by September 1995.

According to the CEN/CENELEC Internal Regulations, the following countries are bound to implement this European Standard: Austria, Belgium, Denmark, Finland, France, Germany, Greece, Iceland, Ireland, Italy, Luxembourg, Netherlands, Norway, Portugal, Spain, Sweden, Switzerland and United Kingdom.

Introduction

The permanganate index is a conventional measure of the contamination by organic and oxidizable inorganic matter in a water sample. It is primarily intended for judging the quality of potable water and raw waters, such as well and surface waters. More heavily contaminated waters may be analysed, provided an appropriate pre-dilution step is adopted. The permanganate index can be determined for waters containing less than 500 mg/l of chloride ion. Reducing compounds such as iron(II) salts, nitrites or hydrogen sulfide may contribute to the permanganate index but are not classified as impurities.

The permanganate index cannot be considered as a measure of the the oretical oxygen demand or the total content of organic matter. Many organic compounds are only partially oxidized in this test, as oxidation is generally incomplete. Volatile matter that evaporates before the addition of permanganate is not included.

The method is not recommended for determining organic load in waste waters; for this purpose the chemical oxygen demand should be determined as described in ISO 6060:1989, *Water quality — Determination of the chemical oxygen demand.*

The method is simple and convenient for surveying the quality of a large number of water samples.

1 Scope

This International Standard specifies a method for the determination of the permanganate index of water. It is primarily intended for water for human consumption and domestic use, drinking water, natural mineral water, well and table water, as well as water from swimming pools. It is used for the determination of the parameter “oxidizability”. It is applicable to waters having a chloride ion concentration of less than 300 mg/l. Samples having a permanganate index over 10 mg/l should be diluted before analysis. The lower limit of the optimum range of the test is 0,5 mg/l.

2 Normative reference

The following standard contains provisions which, through reference in this text, constitute provisions of this International Standard. At the time of publication, the edition indicated was valid. All standards are subject to revision, and parties to agreements based on this International Standard are encouraged to investigate the possibility of applying the most recent edition of the standard indicated below. Members of IEC and ISO maintain registers of currently valid International Standards.

ISO 385-1:1984, *Laboratory glassware — Burettes — Part 1: General requirements.*

3 Definition

3.1
permanganate index (of water)

the mass concentration of oxygen equivalent to the amount of permanganate ion consumed when a water sample is treated with that oxidant under defined conditions

4 Principle

Heating of a sample in a boiling water-bath with a known amount of potassium permanganate and sulfuric acid for a fixed period of time (10 min). Reduction of part of the permanganate by oxidizable material in the sample and determination of the consumed permanganate by addition of an excess of oxalate solution, followed by titration with permanganate.

NOTE 1 The suggested maximum permanganate index of 10 mg/l is equivalent to a consumption of approximately 60 % of the added permanganate by the non-diluted sample.

5 Reagents

During the analysis, use only reagents of recognized analytical grade and only distilled water, water from a reverse osmosis or water of equivalent purity. Do not use deionized water from an organic ion exchanger.

NOTE 2 Non-reducing water can be prepared as follows. Add 10 ml of sulfuric acid (**5.3**) and a small excess of the potassium permanganate stock solution (**5.6**) to 1 litre of distilled water. Distil in an all-glass apparatus and discard the first 100 ml of distillate. Store in a glass bottle with a glass stopper.

The volume of the consumed potassium permanganate standard solution V_0 (see **8.4**) shall not exceed 0,1 ml, otherwise the procedure shall be repeated or a water of lower organic content shall be used.

5.1 *Sulfuric acid*, $\rho(H_2SO_4)$ = 1,84 g/ml, 18 mol/l.

5.2 *Sulfuric acid*, $c(H_2SO_4)$ = 7,5 mol/l.

Add slowly, while stirring continuously, 420 ml of sulfuric acid (**5.1**) to 500 ml of water. Allow to cool and dilute to 1 litre.

5.3 *Sulfuric acid*, $c(H_2SO_4)$ = 2 mol/l.

Add slowly, while stirring continuously, 110 ml of sulfuric acid (**5.1**) to about 500 ml of water. Slowly add potassium permanganate solution (**5.7**) until a faint pink colour persists. Allow to cool, dilute with water to 1 litre and mix.

5.4 *Sodium oxalate*, stock solution, $c(Na_2C_2O_4) = 0{,}05$ mol/l.

Dry sodium oxalate at 120 °C for 2 h. Dissolve 6,700 g of the dried solid in water in a 1 000 ml one-mark volumetric flask. Make up to the mark with water and mix.

This solution is stable for 6 months if stored in a dark place.

5.5 *Sodium oxalate*, standard volumetric solution, $c(Na_2C_2O_4) = 5$ mmol/l.

Pipette 100 ml ± 0,25 ml of the sodium oxalate stock solution (**5.4**) into a 1 000 ml one-mark volumetric flask, make up to the mark with water and mix.

This standard volumetric solution is stable for 2 weeks.

NOTE 3 Commercially available ready-made solutions may be used.

5.6 *Potassium permanganate*, stock solution, $c(KMnO_4) \approx 20$ mmol/l.

Dissolve about 3,2 g of potassium permanganate in water and make up to 1 000 ml. Heat the solution to 90 °C to 95 °C for 2 h, cool and store for not less than 2 days. Decant the clear solution and store in a dark bottle.

5.7 *Potassium permanganate*, volumetric solution, $c(KMnO_4) \approx 2$ mmol/l.

Pipette 100 ml of the potassium permanganate stock solution (**5.6**) into a 1 000 ml, one-mark volumetric flask. Make up to the mark with water and mix.

This volumetric solution is relatively stable for several months if it is stored in the dark. The procedure described in **8.5** automatically allows for its exact concentration to be included in the calculation in **9.1**.

6 Apparatus

Usual laboratory apparatus, and the following should be used

6.1 *Water-bath*, with a rack for test tubes, of sufficient capacity and power to ensure that the solutions in all the test tubes quickly reach and are maintained at a temperature between 96 °C and 98 °C, during both the initial heating and the reaction stages.

6.2 *Test tubes*, of length 150 mm to 200 mm, diameter 25 mm to 35 mm and wall thickness 0,5 mm to 1 mm. Keep the test tubes exclusively for the determination of the permanganate index.

Clean all new test tubes by heating with acidified permanganate solution. This shall be checked by performing blank determinations until the values are adequately low and constant.

A blank value V_0 shall typically not exceed 0,1 ml.

6.3 *Burette*, of capacity 10 ml, preferably of the piston type, graduated in divisions of 0,02 ml, and conforming to the requirements of ISO 385-1.

6.4 *Measuring flasks*, of capacity 100 ml and 1 000 ml.

6.5 *Volumetric pipettes*, of capacity 5 ml, 10 ml, 25 ml, 50 ml, and 100 ml.

7 Sampling and samples

Immediately after receiving the sample in the laboratory, add 5 ml of sulfuric acid (**5.2**) per litre of sample, if this was not done during sampling in the field, regardless of whether the sample is to be stored before analysis.

Analyse the samples as soon as possible and not later than 2 days after sampling. Keep them in the dark at 0 °C to 5 °C if the storage time exceeds 6 h.

Shake the storage bottles and make sure that their contents are well homogenized when withdrawing a test portion for analysis.

8 Procedure

8.1 Check that all flasks and test tubes (**6.2**) used during the procedure are perfectly clean (see **6.2**).

8.2 Dilute samples having a high permanganate index, so that the results for the diluted samples fall within the range 0,5 mg/l to 10 mg/l.

8.3 Pipette 25,0 ml ± 0,25 ml of the test sample (or the diluted test sample) into a test tube. Add 5 ml ± 0,5 ml of sulfuric acid (**5.3**) and mix by swirling gently.

Place the test tube in the boiling water-bath (**6.1**) for 10 min ± 2 min.

Add 5 ml ± 0,05 ml of potassium permanganate volumetric solution (**5.7**) and commence timing.

After 10 min ± 15 s, add 5 ml ± 0,05 ml of the sodium oxalate standard volumetric solution (**5.5**) and wait until the solution is colourless. Titrate, whilst hot, with potassium permanganate volumetric solution (**5.7**) to a faint pink colour which persists for about 30 s. Note the volume V_1 of permanganate solution consumed.

8.4 Carry out a blank test in parallel with the determination, using the same procedure, but replacing the test portion with 25 ml of water. Note the volume V_0 of permanganate solution consumed.

Retain the titrated solution for standardization of the potassium permanganate volumetric solution (**5.7**), as described in **8.5**.

8.5 To the titrated solution retained from the blank test (**8.4**), add 5,00 ml ± 0,05 ml of the sodium oxalate standard volumetric solution (**5.5**). Reheat the solution, if necessary, to about 80 °C and titrate with potassium permanganate volumetric solution (**5.7**) until the appearance of a pink colour which persists for about 30 s. Note the volume V_2 of permanganate solution consumed.

NOTE 4 It is good practice to leave the titrated solutions in the test tubes until they are required for the next determination of permanganate index.

9 Expression of results

9.1 Calculation

Calculate the permanganate index, I_{Mn}, expressed in milligrams of oxygen per litre, using the expression

$$I_{\mathrm{Mn}} = \frac{V_1 - V_0}{V_2} \cdot f \qquad \ldots (1)$$

where

V_0 is the volume, in millilitres, of permanganate solution consumed in the blank titration (**8.4**);

V_1 is the volume, in millilitres, of permanganate solution consumed in the titration of the test portion (**8.3**);

V_2 is the volume, in millilitres, of permanganate solution consumed in the standardization titration (**8.5**);

f is the factor, in milligrams per litre, for recalculation to oxygen and allowing for the sample volume used; f is calculated as follows:

$$f = \frac{V_4 \cdot c(\mathrm{Na_2C_2O_4}) \cdot M_{\mathrm{O}} \cdot 1\,000}{1\,000 \cdot V_5}$$

where

V_4 is the volume, in millilitres, of the sodium oxalate standard volumetric solution (**5.5**) used for the determination according to **8.5** (here: 5);

$c(\mathrm{Na_2C_2O_4})$ is the amount-of-substance concentration, in millimoles per litre, of the sodium oxalate standard volumetric solution (**5.5**) (here: 5);

1 000 (numerator) is the factor for recalculation of $c(\mathrm{Na_2C_2O_4})$, from mmol/l to mmol/ml, in millilitres per litre;

M_{O} is the molar mass, in milligrams of oxygen per millimole, for the recalculation to oxygen (here: 16);

V_5 is the sample volume used, in millilitres (here: 25);

1 000 (denominator) is the factor for recalculation of the measured value to 1 litre of sample volume, in millilitres per litre.

9.2 Precision

9.2.1 *Within-laboratory standard deviation*

Table 1

Sample	Permanganate index found	Standard deviation	Number of degrees of freedom
	mg/l	mg/l	
Tap water[a]	1,28 to 1,94	0,06 to 0,21	10
Resorcinol[b] (1,0 mg/l)	1,63 to 2,04	0,06 to 0,20	10
Resorcinol[b] (6,0 mg/l)	9,32 to 10,28	0,07 to 0,27	10
Various raw and potable waters[c]	0,23 to 8,17	0,05 to 0,60	Various up to 10

[a] Range of results obtained for a distributed tap water analysed in six laboratories. N.B. The range of values found should not be taken to indicate the presence of interlaboratory bias, because of possible sample instability.

[b] Range of results obtained by seven laboratories for a resorcinol solution made up by the individual laboratories from a distributed resorcinol sample.

[c] Range of standard deviations for a variety of raw and potable waters; data obtained from five laboratories.

9.2.2 *Total standard deviation*

Table 2

Sample	Permanganate index found	Standard deviation	Number of degrees of freedom
	mg/l	mg/l	
Resorcinol[a] (1,0 mg/l)	1,83	0,10	20
Resorcinol[a] (6,0 mg/l)	9,95	0,12	23

[a] Total standard deviations obtained by a single laboratory for several batches.

10 Test report

The test report shall include the following information:

a) reference to this International Standard;

b) precise identification of the sample;

c) any pretreatment, such as filtration or sedimentation, which may have influenced the results;

d) the results, to two significant figures and expressed in milligrams per litre;

e) any departure from the procedure specified, any operations regarded as optional, or any other circumstances that may have affected the results.

National annex NA (informative) Committees responsible

The United Kingdom participation in the preparation of this European Standard was entrusted by the Environment and Pollution Standards Policy Committee (EPC/-) to Technical Committee EPC/44 upon which the following bodies were represented:

Association of Consulting Engineers
British Association for Chemical Specialities
British Gas plc
Chemical Industries' Association
Department of the Environment for Northern Ireland
Department of the Environment (Water Directorate)
Department of Trade and Industry (Laboratory of the Government Chemist)
Industrial Water Society
Institute of Petroleum
Institution of Water Officers
Institution of Gas Engineers
Institution of Water and Environmental Management
National Rivers Authority
Royal Institute of Public Health and Hygiene
Royal Society of Chemistry
Scottish Association of Directors of Water and Sewerage Services
Soap and Detergent Industry Association
Water Companies Association
Water Research Centre
Water Services Association of England and Wales

The following bodies were also represented in the drafting of the standard, through subcommittees and panels:

British Agrochemicals Association Ltd.
British Ceramic Research Ltd.
British Laboratory Ware Association Ltd.
British Soft Drinks Association Ltd.
Convention of Scottish Local Authorities
Department of Trade and Industry (Warren Spring Laboratory)
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