BRITISH STANDARD

BS EN ISO 7393-1:2000

BS 6068-2.25:1986

Incorporating Amendment No. 1 to BS 6068-2.25:1986 (renumbers the BS as BS EN ISO 7393-1:2000)

Water quality — Determination of free chlorine and total chlorine —

Part 1: Titrimetric method using *N*,*N*-diethyl-1,4-phenylenediamine

The European Standard EN ISO 7393-1:2000 has the status of a British Standard.

Confirmed
July 2008

ICS 13.060.50

National foreword

This British Standard is the English language version of EN ISO 7393-1:2000. It is identical to ISO 7393-1:1985.

The UK participation in its preparation was entrusted by Technical Committee EH/3, Water quality, to Subcommittee EH/3/2, Physical, Chemical and Biochemical, which has the responsibility to:

- aid enquirers to understand the text;
- present to the responsible international committee any enquiries on interpretation, or proposals for change, and keep UK interests informed;
- monitor related international and European developments and promulgate them in the UK.

A list of organizations represented on this subcommittee can be obtained on request to its secretary.

BS EN ISO 7393-1 is one of a series of standards on water quality, others of which have been, or will be, published as sections of BS 6068. This standard has therefore been given the secondary identifier BS 6068-2.25. The various sections of BS 6068 are comprised within parts 1 to 7, which, together with part 0, are listed below.

— *Part 0: Introduction;*
— *Part 1: Glossary;*
— *Part 2: Physical, chemical and biochemical methods;*
— *Part 3: Radiological methods;*
— *Part 4: Microbiological methods;*
— *Part 5: Biological methods;*
— *Part 6: Sampling;*
— *Part 7: Precision and accuracy.*

The British Standards which implement international or European publications referred to in this document may be found in the BSI Standards Catalogue under the section entitled "International Standards Correspondence Index" or by using the "Find" facility of the BSI Standards Electronic Catalogue.

The method referred to in **4.2**, for the disposal of solutions containing mercury given in ISO 5790 is technically equivalent to that given in the national appendix BS 6070-2, *Methods of sampling and test for sodium carbonate for industrial use — Part 2: Determination of chloride content*.

Textual error. When adopting the text of the international standard, the following textural error was discovered. It has been marked in the text and has been reported to ISO in a proposal to amend the text of the international standard.

In **4.5.2**, the equation should be read as:

$$c_1 = V_2 \frac{c_2}{2V_1}$$

A British Standard does not purport to include all the necessary provisions of a contract. Users of British Standards are responsible for their correct application.

Compliance with a British Standard does not of itself confer immunity from legal obligations.

Summary of pages

This document comprises a front cover, an inside front cover, pages i and ii, the EN ISO title page, the EN ISO foreword page, pages 1 to 8, an inside back cover and a back cover.

The BSI copyright notice displayed in this document indicates when the document was last issued.

This British Standard, having been prepared under the direction of the Environment and Pollution Standards Committee, was published under the authority of the Board of BSI and comes into effect on 28 November 1986

The following BSI references relate to the work on this standard:
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Contents

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EUROPEAN STANDARD
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EN ISO 7393-1

January 2000

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English version

Water quality — Determination of free chlorine and total chlorine — Part 1: Titrimetric method using *N*,*N*-diethyl-1,4-phenylenediamine

(ISO 7393-1:1985)

Qualité de l'eau — Dosage du chlore libre et du chlore total — Partie 1: Méthode titrimétrique à la *N*,*N*-diéthylphénylène-1,4 diamine (ISO 7393-1:1985)

Wasserbeschaffenheit — Bestimmung von freiem Chlor und Gesamtchlor — Teil 1: Titrimetrisches Verfahren mit *N*,*N*-Diethyl-1,4-Phenylendiam (ISO 7393-1:1985)

This European Standard was approved by CEN on 20 January 2000.

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.

This European Standard exists in three official versions (English, French, German). A version in any other language made by translation under the responsibility of a CEN member into its own language and notified to the Central Secretariat has the same status as the official versions.

CEN members are the national standards of Austria, Belgium, Czech Republic, Denmark, Finland, France, Germany, Greece, Iceland, Ireland, Italy, Luxembourg, Netherlands, Norway, Portugal, Spain, Sweden, Switzerland and United Kingdom.

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 7393-1:2000 E

Foreword to EN ISO 7393-1:2000

The text of the International Standard from Technical Committee ISO/TC 147, Water quality, of the International Organization for Standardization (ISO) has been taken over as a European Standard by Technical Committee CEN/TC 230, Water analysis, the Secretariat of which is held by DIN.

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 July 2000, and conflicting national standards shall be withdrawn at the latest by July 2000.

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

0 Introduction

ISO 7393 consists of the following parts.

Part 1: Titrimetric method using *N,N*-diethyl-1,4-phenylenediamine.

Part 2: Colorimetric method using *N,N*-diethyl-1,4-phenylenediamine, for routine control purposes.

Part 3: Iodometric titration method for the determination of total chlorine.[1)]

1 Scope and field of application

This part of ISO 7393 specifies a titrimetric method for the determination of free chlorine and total chlorine in water.

Sea water and waters containing bromides and iodides comprise a group for which special procedures are required.[2]

The method is applicable to concentrations, in terms of chlorine (Cl_2), from 0,000 4 to 0,07 mmol/l (0,03 to 5 mg/l) total chlorine and at higher concentrations by dilution of samples. For concentrations above 0,07 mmol/l, ISO 7393-3 can also be used.

In Annex A a procedure is presented for the differentiation of combined chlorine of the monochloramine type, combined chlorine of the dichloramine type and combined chlorine in the form of nitrogen trichloride.

Several compounds influence the determination specified in this part of ISO 7393. Interferences are noted in clauses **7** and **9**.

2 Definitions (see Table 1)

For the purpose of this part of ISO 7393, the following definitions apply.

2.1
free chlorine

chlorine present in the form of hypochlorous acid, hypochlorite ion or dissolved elemental chlorine

2.2
combined chlorine

the fraction of total chlorine present in the form of chloramines and organic chloramines

2.3
total chlorine

chlorine present in the form of “free chlorine” or “combined chlorine” or both

2.4
chloramines

derivatives of ammonia by substitution of one, two or three hydrogen atoms with chlorine atoms (monochloramine NH_2Cl, dichloramine $NHCl_2$, nitrogen trichloride NCl_3) and all chlorinated derivatives of organic nitrogen compounds as determined by the method specified in this part of ISO 7393

3 Principle

3.1 Determination of free chlorine

Direct reaction with the *N,N*-diethyl-1,4-phenylenediamine (DPD) and formation of a red compound at pH 6,2 to 6,5. Titration by means of a standard solution of ammonium iron(II) sulfate to the disappearance of the red colour.

3.2 Determination of total chlorine

Reaction with DPD in the presence of an excess of potassium iodide then titration as in **3.1**.

4 Reagents

During the analysis, use only reagents of recognized analytical grade, and only water as specified in **4.1**.

Table 1 — Terms and synonyms in relation to actual compounds in the solution

Term	Synonym		Compounds
Free chlorine	Free chlorine	Active free chlorine	Elemental chlorine, hypochlorous acid
		Potential free chlorine	Hypochlorite
Total chlorine	Total residual chlorine		Elemental chlorine, hypochlorous acid, hypochlorite, chloramines

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[1)] At present at the stage of draft.

4.1 *Water,* free from oxidizing and reducing substances.

Demineralized or distilled water of which the quality is checked as follows.

Into two 250 ml chlorine-demand-free conical flasks (clause **5**) place, in order,

a) in the first: 100 ml of the water to be checked and about 1 g of potassium iodide (**4.4**); mix and after 1 min add 5 ml buffer solution (**4.2**) and 5,0 ml of DPD reagent (**4.3**);

b) in the second: 100 ml of the water to be checked and two drops of sodium hypochlorite solution (**4.8**); then, after 2 min, 5,0 ml of buffer solution (**4.2**) and 5 ml of DPD reagent (**4.3**).

No coloration should appear in the first flask whereas it is essential that a light pink coloration appears in the second flask.

In the case of demineralized or distilled water not having the desired quality it must be chlorinated. After a period of contact followed by dechlorination the quality finally has to be rechecked.

A procedure for the preparation of water free from oxidizing and reducing substances is given in Annex B.

4.2 *Buffer solution,* pH 6,5.

Dissolve in water (**4.1**) in this order: 24 g anhydrous disodium hydrogen phosphate (Na_2HPO_4) or 60,5 g of the dodecahydrate form ($Na_2HPO_4 \cdot 12H_2O$) and 46 g of potassium dihydrogen phosphate (KH_2PO_4). Add 100 ml of 8 g/l disodium dihydrogenethylenedinitrilotetraacetate dihydrate (disodium EDTA dihydrate, $C_{10}H_{14}N_2O_8Na_2 \cdot 2H_2O$) solution (or 0,8 g of the solid form).

If necessary, add 0,020 g of mercury(II) chloride ($HgCl_2$), to prevent mould growth and interference in the free available chlorine test caused by any trace amounts of iodide in the reagents.

Dilute to 1 000 ml and mix.

NOTE Solutions containing mercury should be disposed of properly (for example a method is specified in ISO 5790, *Inorganic chemical products for industrial use — General method for determination of chloride content — Mercurimetric method*).

4.3 *N,N-diethyl-1,4-phenylenediamine sulfate (DPD)* $[NH_2\text{-}C_6H_4\text{-}N(C_2H_5)_2.H_2SO_4]$, solution, 1,1 g/l.

Mix 250 ml water (**4.1**), 2 ml sulfuric acid (ϱ = 1,84 g/ml) and 25 ml of 8 g/l disodium EDTA dihydrate solution (or 0,2 g of the solid form). Dissolve in this mixture 1,1 g of anhydrous DPD or 1,5 g of the pentahydrate form, dilute to 1 000 ml and mix.

Store the reagent in a dark bottle protected from heat.

Renew the solution after 1 month or when it becomes discoloured.

4.4 *Potassium iodide,* crystals.

NOTE Reagents **4.2**, **4.3** and **4.4** may be conveniently replaced by combined reagents commercially available in the form of stable powder or tablets.

4.5 *Ammonium iron(II) sulfate,* stock solution, $c[(NH_4)_2Fe(SO_4)_2 \cdot 6H_2O]$ = 0,056 mol/l.

4.5.1 *Preparation of the solution*

Dissolve 22 g of ammonium iron(II) sulfate hexahydrate (Mohr's salt) in about 250 ml water (**4.1**) containing 5 ml sulfuric acid (ϱ = 1,84 g/ml) in a 1 000 ml one-mark volumetric flask. Make up to the mark with water and mix.

Store in a dark bottle.

Standardize this solution by means of the procedure given in **4.5.2**, when required for use, or daily if large numbers of determinations have to be done.

4.5.2 *Standardization of the solution*

Place in a 250 ml conical flask, 50,0 ml of the stock solution (**4.5.1**), about 50 ml water (**4.1**), 5 ml orthophosphoric acid (ϱ = 1,71 g/ml) and 4 drops of barium diphenylamine sulfonate indicator (**4.9**). Titrate with potassium dichromate solution (**4.10**). The end-point is reached when one drop produces an intense purple coloration which remains unchanged after further addition of the potassium dichromate solution. The concentration, c_1, expressed in millimoles of Cl_2 per litre, of this solution is given by the equation[2]

$$c_1 = V_2 \frac{c_2}{V_1}$$

where

c_2 is the concentration of the potassium dichromate standard reference solution (**4.10**),$c(1/6\ K_2Cr_2O_7)$ = 100 mmol/l;

V_1 is the volume, in millilitres, of ammonium iron(II) sulfate stock solution (**4.5**), 50,0 ml;

V_2 is the volume, in millilitres, of the potassium dichromate standard reference solution (**4.10**) used in the titration.

NOTE When V_2 becomes less than 22 ml, prepare a fresh stock solution (see **4.5.1**).

4.6 *Ammonium iron(II) sulfate,* standard volumetric solution, $c[(NH_4)_2Fe(SO_4)_2 \cdot 6H_2O]$ = 2,8 mmol/l.

Place 50,0 ml of the freshly standardized stock solution (**4.5.1**) in a 1 000 ml one-mark volumetric flask. Make up to the mark with water (**4.1**) and mix.

Transfer to a dark bottle.

Prepare this solution when required for use, or daily if large numbers of determinations have to be done.

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[2] See national foreword for details of textural error.

The concentration, c_3, expressed in millimoles of Cl_2 per litre, of this solution is given by the equation

$$c_3 = \frac{c_1}{20}$$

where c_1 is as defined in **4.5.2**.

4.7 *Sodium arsenite* ($NaAsO_2$), solution, 2 g/l; or *thioacetamide* (CH_3CSNH_2), solution, 2,5 g/l.

4.8 *Sodium hypochlorite,* solution [$\varrho(Cl_2)$ about 0,1 g/l].

Prepare by dilution of concentrated commercial sodium hypochlorite solution.

4.9 *Barium diphenylamine sulfonate,* indicator solution, 3 g/l.

Dissolve 0,3 g barium diphenylamine sulfonate [$(C_6H_5\text{-}NH\text{-}C_6H_4\text{-}SO_3)_2Ba$] in 100 ml water.

4.10 *Potassium dichromate,* standard reference solution, $c(1/6\ K_2Cr_2O_7)$ = 100 mmol/l.

Weigh, to the nearest milligram, 4,904 g of anhydrous potassium dichromate. Dissolve in water in a 1 000 ml one-mark volumetric flask. Make up to the mark with water and mix.

5 Apparatus

Ordinary laboratory apparatus, and

Microburette, measuring up to 5 ml and graduated in divisions of 0,02 ml.

NOTE ON THE PREPARATION OF GLASSWARE

Chlorine-demand-free glassware is obtained by filling with sodium hypochlorite solution (**4.8**) then, after 1 h, rinsing copiously with water (**4.1**). During the course of the analysis one set of glassware should be kept for the determination of free chlorine and another for the determination of total chlorine in order to avoid contamination of the free chlorine set.

6 Procedure

6.1 Test sample

Start determination immediately after taking samples. At all times avoid bright light, agitation and heat.

6.2 Test portions

Take two test portions, each of 100,0 ml. If the concentration of total chlorine exceeds 70 µmol/l (5 mg/l) it is necessary to take a smaller volume of test sample and to dilute with water (**4.1**) to 100,0 ml.

6.3 Determination of free chlorine

Place rapidly in a 250 ml conical flask in this order: 5,0 ml of buffer solution (**4.2**), 5,0 ml of DPD reagent (**4.3**) and the first test portion (**6.2**). Mix and titrate immediately to a colourless end-point with ammonium iron(ll) sulfate solution (**4.6**). Note the volume, V_3, in millilitres, used in the titration.

In the case of an unknown water, possibly being very acid, or very alkaline or with a high concentration of salts, it is advisable to verify that the volume of buffer solution (**4.2**) added is sufficient to bring the water to pH 6,2 to 6,5. If not, use a greater volume of the buffer solution (**4.2**).

6.4 Determination of total chlorine

Place rapidly in a 250 ml conical flask in this order: 5,0 ml of buffer solution (**4.2**), 5,0 ml of DPD reagent (**4.3**), the second test portion (**6.2**) and about 1 g of potassium iodide (**4.4**). Mix and after 2 min, titrate to a colourless end-point with the ammonium iron(II) sulfate solution (**4.6**). If within 2 min a drift back of colour is observed continue titration to a colourless end-point. Note the volume, V_4, in millilitres, used in the titration.

In the case of an unknown water, possibly being very acid, or very alkaline or with a high concentration of salts, it is advisable to verify that the volume of buffer solution (**4.2**) added is sufficient to bring the water to pH 6,2 to 6,5. If not, use a greater volume of the buffer solution (**4.2**).

7 Correction of interference due to the presence of oxidized manganese

Determine the effect of oxidized manganese by carrying out a supplementary determination on a further test portion (**6.2**) previously treated with the arsenite or thioacetamide solution (**4.7**) in order to neutralize all oxidizing compounds other than oxidized manganese.

Place this test portion in a 250 ml conical flask, add 1 ml of sodium arsenite solution (**4.7**) or thioacetamide solution (**4.7**) and mix. Again add 5,0 ml of buffer solution (**4.2**) and 5,0 ml of DPD reagent (**4.3**). Titrate immediately to a colourless end-point against ammonium iron(II) sulfate solution (**4.6**). Note the volume, V_5, in millilitres, corresponding to the oxidized manganese.

8 Expression of results

8.1 Method of calculation

8.1.1 *Calculation of the free chlorine concentration*

The concentration of free chlorine, $c(\mathrm{Cl_2})$, expressed in millimoles per litre, is given by the equation

$$c(\mathrm{Cl_2}) = \frac{c_3(V_3 - V_5)}{V_0}$$

where

c_3 is the concentration, expressed in millimoles of $\mathrm{Cl_2}$ per litre, of ammonium iron(II) sulfate solution;

V_0 is the volume, in millilitres, of test sample in the test portion (**6.2**);

V_3 is the volume, in millilitres, of the ammonium iron(II) sulfate solution (**4.6**) used in the titration (**6.3**);

V_5 is the volume, in millilitres, of the ammonium iron(II) sulfate solution (**4.6**) used in clause **7** (V_5 = 0 ml in the absence of oxidized manganese).

8.1.2 *Calculation of the total chlorine concentration*

The concentration of total chlorine, $c(\mathrm{Cl_2})$, expressed in millimoles per litre, is given by the equation

$$c(\mathrm{Cl_2}) = \frac{c_3(V_4 - V_5)}{V_0}$$

where

c_3 V_0 and V_5 are as defined in **8.1.1**;

V_4 is the volume, in millilitres, of the ammonium iron(II) sulfate solution (**4.6**) used in the titration (**6.4**).

8.2 Conversion of amount of substance concentration to mass concentration

The chlorine concentration expressed in moles per litre may be expressed in grams per litre by multiplying by a conversion factor of 70,91.

8.3 Repeatability and reproducibility

To obtain an indication of repeatability and reproducibility, figures are taken from measurements obtained by methods which are the same in principle as that specified in this part of ISO 7393.

The USA-EPA Environmental Monitoring and Support Laboratory[1] evaluated the titrimetric method with the following results.

For distilled water samples at concentrations of $c(\mathrm{Cl_2})$ = 4,79; 9,17; and 48,6 µmol/l [$\varrho(\mathrm{Cl_2})$ = 0,34; 0,65; and 3,45 mg/l] total chlorine, the relative standard deviations were 5,6 %, 0,5 % and 0,5 %, respectively. Using drinking water containing $c(\mathrm{Cl_2})$ = 13,8 µmol/l [$\varrho(\mathrm{Cl_2})$ = 0,98 mg/l], total chlorine, the relative standard deviation was 1,2 %. With more polluted waters almost the same precision was obtained as for drinking water with the exception of raw sewage where, with a total chlorine concentration of $c(\mathrm{Cl_2})$ = 11,1 µmol/l [$\varrho(\mathrm{Cl_2})$ = 0,79 mg/l], the relative standard deviation was 3,3 %.

Results published by the British Department of the Environment[2] showed for total chlorine concentrations of $c(\mathrm{Cl_2})$ = 14 and 71 µmol/l [$\varrho(\mathrm{Cl_2})$ = 1,0 and 5,0 mg/l], relative standard deviations of 1,4 % and 0,88 %, respectively.

The results presented in the preceding paragraphs relate to replicate determinations in the same laboratory and thus provide a measure of the repeatability of the method. Attempts in the past to quantify the reproducibility of the method by distribution of samples to different laboratories have produced unreliable results because of a general instability of solutions containing free and combined chlorine. More recently it has been found by the Quality Assurance Branch of EMSL-Cincinnati[5] that a sealed vial of sodium hypochlorite in very pure water is remarkably stable when stored in the dark inside a mailing tube. Subsequent evaluation by various US federal and state laboratories has produced the analytical parameters listed in Table 2 for methods in current use.

9 Interferences

Two types of interference may be noted.

9.1 Interference by other chlorine compounds

A fraction of any chlorine dioxide that might be present is measured as free chlorine. This interference may be corrected by determining the chlorine dioxide in the water.[2, 3, 4]

Table 2 — Analytical parameters from interlaboratory analysis for free residual chlorine

True value $c(Cl_2)$	True value $[\varrho(Cl_2)]$	Method code[a]	Number of laboratories (observations)	Mean	Mean	Standard deviation	Standard deviation
µmol/l	(mg/l)			µmol/l	(mg/l)	µmol/l	(mg/l)
7	(0,5)	A	6	6,2	(0,44)	1,3	(0,09)
		B	7	6,8	(0,48)	1,8	(0,13)
11,3	(0,80)	A	10	10,9	(0,77)	1,1	(0,08)
		B	14	11,1	(0,79)	4,1	(0,29)
		C	6	11,6	(0,82)	1,3	(0,09)
15,5	(1,10)	A	10	15,5	(1,10)	2,0	(0,14)
		B	14	16,2	(1,15)	5,5	(0,39)
		C	6	16,5	(1,17)	1,1	(0,08)
18,2	(1,29)	A	6	18,6	(1,32)	1,3	(0,09)
		B	7	19,9	(1,41)	5,4	(0,38)

[a] A: Iodometric titration amperometric
B: DPD colorimetric
C: DPD titrimetric

9.2 Interference by compounds other than chlorine compounds

Oxidation of DPD is not specifically caused by chlorine compounds. Depending on the concentration and the chemical oxidation potential, the reaction is effected by other oxidizing agents. The following substances may be mentioned in particular: bromine, iodine, bromamines, iodoamines, ozone, hydrogen peroxide, chromate, oxidized manganese, nitrite, iron(III) ions and copper ions. The interference is suppressed by the disodium EDTA in reagents **4.2** and **4.3** in the case of copper(II) ions (< 8 mg/l) and iron(III) ions (< 20 mg/l).

Interference by chromate may be eliminated by addition of barium chloride.[6]

10 Test report

The test report shall include the following information:

a) a reference to this part of ISO 7393;

b) all information necessary for complete identification of the sample;

c) the results and the method of expression used;

d) details of any operations not included in this part of ISO 7393, or regarded as optional, together with any circumstance that may have affected the results.

Annex A Separate determinations of combined chlorine of the monochloramine type, combined chlorine of the dichloramine type and of combined chlorine in the form of nitrogen trichloride

A.1 Applicability

This annex specifies a method for the differentiation between combined chlorine of the monochloramine type, combined chlorine of the dichloramine type and combined chlorine in the form of nitrogen trichloride. The field of application of the method is the same as that for concentrations of free chlorine and total chlorine (see clause **1**).

A.2 Principle

After determination of free chlorine and total chlorine, titration of two further test portions:

a) on the third test portion: reaction with DPD limited to free chlorine and to combined chlorine of the monochloramine type by the addition of a small quantity of potassium iodide;

b) on the fourth test portion, by addition of a small quantity of potassium iodide before the addition of buffer and DPD reagent: reaction with DPD by free chlorine, by combined chlorine of the monochloramine type and one half of the nitrogen trichloride.

Combined chlorine of the dichloramine type does not react in either of these two cases. Calculation of the concentration of combined chlorine of the monochloramine and dichloramine types and the concentration of nitrogen trichloride.

A.3 Reagents

The reagents given in clause **4** and

Potassium iodide, solution, 5 g/l.

Prepare this solution on the day of use and store in a brown bottle.

A.4 Apparatus

See clause **5**.

A.5 Procedure

A.5.1 *Test sample*

See **6.1**.

A.5.2 *Test portions*

Work on two test portions similar to those in **6.2**.

A.5.3 *Determination of free chlorine and combined chlorine of the monochloramine type*

Place rapidly in a 250 ml conical flask in this order: 5,0 ml of buffer solution (**4.2**), 5,0 ml of DPD reagent (**4.3**), the third test portion and two drops (about 0,1 ml) of potassium iodide solution (clause **A.3**) or a very small crystal of potassium iodide (about 0,5 mg) and mix. Titrate immediately to a colourless end-point with ammonium iron(II) sulfate solution (**4.6**). Note the volume, V_6, in millilitres, used in the titration.

A.5.4 *Determination of free chlorine, combined chlorine of the monochloramine type and one half of the nitrogen trichloride*

Place in a 250 ml beaker, the fourth test portion and two drops (about 0,1 ml) of potassium iodide solution (clause **A.3**) or a very small crystal of potassium iodide (about 0,5 mg) and mix. Transfer the contents of the beaker to a 250 ml conical flask containing 5,0 ml of buffer solution (**4.2**) and 5,0 ml of DPD reagent (**4.3**) added less than 1 min prior to the transfer. Titrate immediately to a colourless end-point with ammonium iron(II) sulfate solution (**4.6**). Note the volume, V_7, in millilitres, used in the titration.

A.6 Expression of results

A.6.1 *Method of calculation*

A.6.1.1 *Calculation of the concentration of combined chlorine of the monochloramine type*

The concentration of combined chlorine of the monochloramine type, $c(\mathrm{Cl_2})$, expressed in millimoles per litre, is given by the equation

$$c(\mathrm{Cl_2}) = \frac{c_3(V_6 - V_3)}{V_0}$$

where

c_3 V_0 and V_3 are as defined in clause **8**;

V_6 is the volume, in millilitres, of the ammonium iron(II) sulfate solution (**4.6**) used in the titration (**A.5.3**).

A.6.1.2 *Calculation of the concentration of combined chlorine of the dichloramine type*

The concentration of combined chlorine of the dichloramine type, $c(\mathrm{Cl_2})$, expressed in millimoles per litre, is given by the equation

$$c(\mathrm{Cl_2}) = \frac{c_3(V_4 - 2V_7 + V_6)}{V_0}$$

where

c_3, V_0 and V_4 are as defined in clause **8**;

V_6 is as defined in **A.6.1.1**;

V_7 is the volume, in millilitres, of the ammonium iron(II) sulfate solution (**4.6**) used in the titration (**A.5.4**).

A.6.1.3 *Calculation of the concentration of combined chlorine in the form of nitrogen trichloride*

The concentration of combined chlorine in the form of nitrogen trichloride, $c(\mathrm{Cl_2})$, expressed in millimoles per litre, is given by the equation

$$c(\mathrm{Cl_2}) = \frac{2\,c_3(V_7 - V_6)}{V_0}$$

where

c_3 and V_0 are as defined in clause **8**;

V_6 is as defined in **A.6.1.1**;

V_7 is as defined in **A.6.1.2**.

A.6.2 ***Conversion of amount of substance concentration to mass concentration***

The chlorine concentration expressed in moles per litre may be expressed in grams per litre by multiplying by a conversion factor of 70,91.

Annex B Preparation of water free from oxidizing and reducing substances

To obtain dilution water of the desired quality, demineralized or distilled water is first chlorinated to a level of about 0,14 mmol/l (10 mg/l) and stored in a well-stoppered carboy for at least 16 h. The water is then dechlorinated by exposure to UV irradiation, sunlight for several hours or by contact with active carbon. Finally check the quality using the procedures as in **4.1**.

Bibliography

[1] BENDER, D.F. Comparison of methods for the determination of total available residual chlorine in various sample matrices, Report No.
EPA-600/4-78-019. Cincinnati, Ohio 45268, USA, US Environmental Protection Agency, 1978.

[2] DoE. *Chemical Disinfecting Agents in Waters, and Effluents, and Chlorine Demand, Methods for the Examination of Waters and Associated Materials.* London, UK, HMSO, 1980.

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