भारतीय मानक
Indian Standard

IS 3025 (Part 26) : 2021

जल एवं अपशिष्ट जल के नमूने लेने तथा परीक्षण (भौतिक एवं रसायन) की पद्धतियां

भाग 26 क्लोरीन, रेसिडुअल

(दूसरा पुनरीक्षण)

Methods of Sampling and Test (Physical and Chemical) for Water and Waste Water

Part 26 Chlorine, Residual

(Second Revision)

ICS 13.060.50

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Water Quality Sectional Committee, CHD 36

FOREWORD

This Indian Standard (Second Revision) was adopted by the Bureau of Indian Standards, after the draft finalized by the Water Quality Sectional Committee had been approved by the Chemical Division Council.

Chlorination of water and wastewater serves primarily to destroy or deactivate disease-producing micro-organisms. The other benefit is the overall improvement in water quality. Chlorination may produce adverse effects. Taste and odour characteristics of phenols and other organic compounds present in water may be intensified. Potentially carcinogenic chloro-organic compounds, such as chloroform may be formed. Combined chlorine formed on chlorination of ammonia or amine bearing waters adversely affects some aquatic life. To fulfil the primary purpose of chlorination and to minimize any adverse effects, it is essential that proper test methods be used with a fore knowledge of limitations of analytical determination.

This standard superseded 45 of IS 3025 : 1964 and was published as first revision in 1986. In this second revision, due to focus on green chemistry, the following changes has been made:

a) Stabilzed neutral ortho-toluidine method removed;
b) Titrimetric method using *N*,*N*-diethyl-1,4-phenylenediamine added (equivalent to ISO 7393-1 : 1985);
c) Colorimetric method using *N*,*N*-diethyl-1,4-phenylenediamine, for routine control purposes added (equivalent to ISO 7393-2 : 2017); and
d) Interlaboratory repeatability and reproducibility data incorporated for DPD methods.

The composition of the committee, responsible for the formulation of this standard is given at Annex E.

In reporting the results of a test or analysis in accordance with this standard, if the final value observed or calculated, is to be rounded off, it shall be done in accordance with IS 2 : 1960 'Rules for rounding off numerical values (*revised*)'.

Indian Standard

METHODS OF SAMPLING AND TEST (PHYSICAL AND CHEMICAL) FOR WATER AND WASTE WATER

PART 26 CHLORINE, RESIDUAL

(Second Revision)

1 SCOPE

This Indian Standard (Part 26) prescribes the following methods for determination of residual chlorine in water and wastewater:

a) Iodometric method;
b) Titrimetric method using DPD; and
c) Colorimetric method using DPD, for routine control purposes.

2 REFERENCES

The following standards contain provisions which through reference in this text constitute provisions of this standard. At the time of publications, the editions indicated were valid. All standards are subject to revision and parties to agreements based on this standard are encouraged to investigate the possibility of applying the most recent editions of the standards indicated below:

IS No./International Standard	*Title*
695 : 1986	Acetic acid
1070 : 1992	Reagent grade water
2263 : 1979	Methods of preparation of indicator solutions
3025 (Part 1) : 1987	Methods of sampling and test (physical and chemical) for water and wastewater: Part 1 Sampling
ISO 8466-1 : 1990	Water quality — Calibration and evaluation of analytical methods and estimation of performance characteristics — Part 1: Statistical evaluation of the linear calibration function
IS 5182 (Part 2) : 2001	Methods for measurement of air pollution: Part 2 Sulphur dioxide, Section 1 Tetrachloromercurate/pararosaniline method (*second revision*)

3 TERMINOLOGY

For the purpose of this standard, the following definitions shall apply (*see also* Table 1).

3.1 Free Chlorine — Chlorine present in the form of hypochlorous acid, hypochlorite ion or dissolved elemental chlorine.

3.2 Combined Chlorine — The fraction of total chlorine (*see* **3.3**) present in the form of chloramines and organic chloramines.

3.3 Total Chlorine — Chlorine present in the forms of free chlorine (*see* **3.1**) or combined chlorine (*see* **3.2**) or both.

3.4 Chloramines — Derivatives of ammonia by substitution of one, two or three hydrogen atoms with chlorine atoms (monochloramine NH_2Cl, dichloramine $NHCl_2$, nitrogen trichloride NCI_3) and all chlorinated derivatives of organic nitrogen compounds as determined by this method.

4 SAMPLING AND STORAGE

Chlorine is not stable in aqueous solution. Exposure to sunlight or other light or agitation will accelerate the reduction of chlorine. Therefore, it is recommended that chlorine determinations be started immediately after sampling and exposure to light and agitation are to be avoided. The sample cannot be stored. Sampling and storage shall be done as prescribed in IS 3025 (Part 1).

5 IODOMETRIC METHOD

5.1 Applicability

This method is precise when residual concentration exceeds 1 mg/l, but for lower concentrations it is not so accurate.

5.2 Interferences

Oxidized forms of manganese and other oxidizing agents interfere. Reducing agents, such as organic sulphides also interfere. Although the neutral titration minimizes the interfering effect of ferric and nitrate ions, the acid titration is preferred because some forms of combined chlorine do not react at *p*H 7. Use only acetic acid for titration; sulphuric acid will increase interferences; never use hydrochloric acid.

5.3 Reagents

Unless otherwise stated the reagents shall be of analytical reagent grade.

5.3.1 *Acetic Acid, Gglacial*, *See* IS 695.

5.3.2 *Potassium Iodide*, crystals.

5.3.3 *Standard Sodium Thiosulphate*, 0.01 N.

5.3.4 *Starch Indicator Solution*, *see* IS 2263.

5.4 Procedure

5.4.1 Select a sample volume which will require no more than 20 ml of 0.01 N sodium thiosulphate (*see* **5.3.3**). Thus for residual chlorine concentration of 1 mg/l or less, take 1 000 ml of sample; for range of 1 to 10 mg/l, a 500 ml of sample and above 10 mg/l proportionately less sample.

5.4.2 Take appropriate volume of the sample as given in **5.4.1** and add acetic acid to bring down the *p*H to 3 - 4 in the flask. Add about 1.0 g of potassium iodide crystals and mix with a glass rod. Add chlorine-free distilled water if larger volume is preferred for titration. Titrate with 0·01 N sodium thiosulphate (*see* **5.3.3**) until yellow colour of the liberated iodine is almost discharged. Add 1·0 ml of starch indicator (*see* **5.3.4**) and titrate until the blue colour is discharged. In many cases residual chlorine is very low and starch needs to be added before starting up the titration.

5.4.3 *Calculation*

$$\text{Residual chlorine in mg/l} = \frac{V_1 \times N \times 35450}{V_2}$$

where

V_1 = volume of standard sodium thiosulphate used,
V_2 = volume of sample taken for test, and
N = normality of sodium thiosulphate used.

6 TITRIMETRIC METHOD USING DPD

6.1 Applicability

This 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. Sea water and waters containing bromides and iodides comprise a group for which special procedures are required.[1]

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 using this method. Interferences are noted in **6.3** and **6.7**.

Table 1 Terms and Synonyms in Relation to Actual Compounds in the Solution

(*Clause* 3)

Sl No.	Term	Synonym		Compounds
(1)	(2)	(3)		(4)
i)	Free chlorine	Free chlorine	Active free chlorine	Elemental chlorine, hypochlorous acid
			Potential free chlorine	Hypochlorite
ii)	Total chlorine	Total residual chlorine		Elemental chlorine. Hypochlorous acid. hypochlorite, chloramines
iii)	Bound chlorine	Combined chlorine		Difference of total and free chlorine

6.2 Principle

6.2.1 *Determination of Free Chlorine*

Direct reaction with the *N*,*N*-diethyl-1,4-phenylenediamine (DPD) and formation of a red compound at *p*H **6.2** to **6.5**. Titration by means of a standard solution of ammonium iron(ll) sulphate to the disappearance of the red colour.

6.2.2 *Determination of Total Chlorine*

Reaction with DPD in the presence of an excess of potassium iodide then titration as in **6.2.1**.

6.3 Interferences

Two types of interference may be noted.

6.3.1 *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.[2,4-5]

6.3.2 *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(Ill) ions and copper ions. The interference is suppressed by the disodium EDTA in reagents **6.4.2** and **6.4.3** in the case of copper(ll) ions (< 8 mg/l) and iron (lll) ions (< 20 mg/l).

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

6.4 Reagents

During the analysis, use only reagents of analytical grade, and only water as specified in **6.4.1**.

6.4.1 *Water*, as specified in IS 1070, Grade 2, free from oxidizing and reducing substances. Demineralized or distilled water of which the quality is checked as follows.

6.4.1.1 Into two 250 ml chlorine-demand-free conical flasks (*See* **6.5**) place, in order:

a) In the first: 100 ml of the water to be checked and about 1 g of potassium iodide (*See* **6.4.4**); mix and after 1 min add 5.0 ml buffer solution (*See* **6.4.2**) and 5.0 ml of DPD reagent (*see* **6.4.3**).

b) In the second: 100 ml of the water to be checked and two drops of sodium hypochlorite solution (*see* **6.3.8**); then, after 2 min, 5.0 ml of buffer solution (*See* **6.4.2**) and 5.0 ml of DPD reagent (*see* **6.4.3**).

6.4.1.2 No colouration should appear in the first flask whereas it is essential that a light pink colouration appears in the second flask. If the demineralized or distilled water does not have the desired quality, it shall be chlorinated according to the following procedure.

a) First, chlorinate the demineralized or distilled water to a level of about 0.14 mmol/l (10 mg/l) and store it in a well-stoppered carboy for at least 16 h.

b) Then decholorinate the water by exposure to UV irradiation, sunlight for several hours or by contact with active carbon.

c) Finally, check the quality using the procedures as given in **6.6**. The user has to make sure that the glassware is also chlorine demand free. The procedure is described in **6.5.1**.

d) Recheck the quality after a period of contact followed by dechlorination.

6.4.2 *Buffer Solution*, *p*H 6.5.

Dissolve in water (*See* **6.4.1**) in this order: 24 g anhydrous disodium hydrogen phosphate (Na_2HPO_4) or 60.5 g of the dodecahydrate form ($Na_2HPO_4.12H_2O$) and 46 g of potassium dihydrogen phosphate (KH_2PO_4). Add 100 ml of 8 g/l disodium dihydrogenethylene dinitrilotetraacetate dihydrate (disodium EDTA dihydrate, $C_{10}H_{14}N_2O_8Na_2.2H_2O$) solution (or 0.8 g of the solid form).

If necessary, add 0.020 g of mercury(ll) 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 treated to recover mercury and then it should be disposed as per disposal policy for solid waste in India. See **12** of IS 5182 (Part 2) for treatment of mercury containing solutions.

6.4.3 *N,N-diethyl-1,4-phenylenediamine sulphate (DPD)* [NH_2-C_6H_4-$N(C_2H_5)_2.H_2SO_4$], solution, 1.1 g/l.

Mix 250 ml water (*See* **6.4.1**), 2 ml sulphuric 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.

6.4.4 *Potassium Iodide*, Crystals.

NOTE — Reagents **6.4.2**, **6.4.3** and **6.4.4** may be conveniently replaced by combined reagents commercially available in the form of stable powder or tablets.

6.4.5 *Ammonium iron*(ll) *sulphate*, stock solution,

$c[(NH_4)_2Fe(SO_4)_2.6H_2O]$ = 0.056 mol/l.

6.4.5.1 *Preparation of the solution*

Dissolve 22 g of ammonium iron(II) sulfate hexahydrate (Mohr's salt) in about 250 ml water (*see* **6.4.1**) containing 5 ml sulphuric 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 **6.4.5.2**, when required for use, or daily if large numbers of determinations have to be done.

6.4.5.2 *Standardization of the solution*

Place in a 250 ml conical flask, 50.0 ml of the stock solution (*see* **6.4.5**), about 50 ml water (*see* **6.4.1**), 5 ml orthophosphoric acid (ρ = 1.71 g/ml) and 4 drops of barium diphenylamine sulfonate indicator (*see* **6.4.9**). Titrate with potassium dichromate solution (*See* **6.4.10**). 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:

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

where

c_2 = concentration of the potassium dichromate standard reference solution (**6.4.10**), $c(1/6\ K_2Cr_2O_7)$ = 100 mmol/l;

V_1 = volume, in millilitres, of ammonium iron(ll) sulfate stock solution (**6.4.5**), 50.0 ml;

V_2 = volume, in millilitres, of the potassium dichromate standard reference solution (**6.4.10**) used in the titration.

NOTE — When V_2 becomes less than 22 ml, prepare a fresh stock solution (*see* **6.4.5.1**).

6.4.6 *Ammonium Iron*(ll) *sulphate,* standard volumetric solution, $c[(NH_4)_2Fe(SO_4)_2.6H_2O]$ = 2.8 mmol/l.

Place 50.0 ml of the freshly standardized stock solution (*see* **6.4.5**) in a 1 000 ml one-mark volumetric flask. Make up to the mark with water (*see* **6.4.1**) 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.

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 **6.4.5.2**.

6.4.7 *Sodium Arsenite* ($NaAsO_2$), solution, 2 g/l; or thioacetamide (CH_3CSNH_2), solution, 2.5 g/l.

6.4.8 *Sodium Hypochlorite*, solution [$\rho(C1_2)$ about 0.1 g/l].

Prepare by dilution of concentrated commercial sodium hypochlorite solution.

6.4.9 *Barium Diphenylamine Sulphonate*, indicator solution, 3 g/l.

Dissolve 0.3 g barium diphenylamine sulphonate $[(C_6H_5\text{-}NH\text{-}C_6H_4\text{-}SO_3)_2Ba]$ in 100 ml water.

6.4.10 *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 (*see* **6.4.1**) in a 1 000 ml one-mark volumetric flask. Make up to the mark with water and mix.

6.5 Apparatus

Ordinary laboratory apparatus.

6.5.1 *Microburette*, measuring up to 5 ml and graduated in divisions of 0.02 ml.

NOTE — Chlorine-demand-free glassware is obtained by filling with sodium hypochlorite solution (*see* **6.4.8**) then, after 1 h, rinsing copiously with water (*see* **6.4.1**). 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.

6.6 Procedure

6.6.1 *Test Sample*

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

6.6.2 *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 (*see* **6.4.1**) to 100.0 ml.

6.6.3 *Determination of Free Chlorine*

Place rapidly in a 250 ml conical flask in this order: 5.0 ml of buffer solution (*see* **6.4.2**), 5.0 ml of DPD reagent (*see* **6.4.3**) and the first test portion (*see* **6.6.2**). Mix and titrate immediately to a colourless end-point with ammonium iron(II) sulfate solution (*See* **6.4.6**). Note the volume, V_3, in millilitres, used in the titration.

In the case of an unknown water sample, possibly being very acidic, or very alkaline or with a high concentration of salts, it is advisable to verify that the volume of buffer solution (*see* **6.4.2**) added is sufficient to bring the water to *p*H 6.2 to 6.5. If not, use a greater volume of the buffer solution.

6.6.4 *Determination of Total Chlorine*

Place, rapidly in a 250 ml conical flask in this order: 5.0 ml of buffer solution (*see* **6.4.2**), 5.0 ml of DPD reagent (*see* **6.4.3**), the second test portion (*see* **6.6.2**) and about 1 g of potassium iodide (*see* **6.4.4**). Mix and after 2 min, titrate to a colourless end-point with the ammonium iron(ll) sulfate solution (*see* **6.4.6**). 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 sample, possibly being very acidic, or very alkaline or with a high concentration of salts, it is advisable to verify that the volume of buffer solution (*see* **6.4.2**) added is sufficient to bring the water to *p*H 6.2 to 6.5. If not, use a greater volume of the buffer solution.

6.7 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 (*see* **6.6.2**) previously treated with the arsenite or thioacetamide solution (*see* **6.4.7**) 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 (*see* **6.4.7**) or thioacetamide solution (*see* **6.4.7**) and mix. Again add 5.0 ml of buffer solution (*see* **6.4.2**) and 5.0 ml of DPD reagent (*see* **6.4.3**). Titrate immediately to a colourless end-point against ammonium iron(II) sulfate solution (*see* **6.4.6**). Note the volume, V_5, in ml, corresponding to the oxidized manganese.

6.8 Calculation

6.8.1 *Calculation of Free Chlorine Concentration*

The concentration of free chlorine, $c\ (\mathrm{Cl}_{2,\ \mathrm{free}})$, in mmol/l

$$= \frac{c_3\left(V_3 - V_5\right)}{V_0}$$

where

c_3 = concentration, expressed in mmol of Cl_2 per litre, of ammonium iron(ll) sulfate solution;

V_o = volume of test sample in the test portion (**6.6.2**), in ml;

V_3 = volume of the ammonium iron(ll) sulfate solution (**6.4.6**) used in the titration (**6.6.3**), in ml; and

V_5 = volume of the ammonium iron(ll) sulfate solution (**6.4.6**) used in **6.7** (V_5 = 0 ml in the absence of oxidized manganese), in ml.

6.8.2 *Calculation of the Total Chlorine Concentration*

The concentration of total chlorine, $c\ (\mathrm{Cl}_{2,\ \mathrm{total}})$, in

$$\text{mmol/l} = \frac{c_3\left(V_4 - V_5\right)}{V_0}$$

where

c_3, V_0 and V_5 are as defined in **6.8.1**; and

V_4 = of the ammonium iron(II) sulfate solution (*See* **6.4.6**) used in the titration (*See* **6.6.4**), in ml.

6.8.3 *Conversion into Mass Units*

The chlorine concentration expressed in mmol/l may be expressed in mg/l by multiplying by a conversion factor of 70.91.

6.8.4 *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 method.

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 [$\rho(\mathrm{Cl}_2)$ = 0.34; 0.65; and 3.45 mg/l] total chlorine, the relative standard deviations were 5.6 percent, 0.5 percent and 0.5 percent, respectively. Using drinking water containing $c(\mathrm{Cl}_2)$ = 13.8 µmol/l [$\rho(\mathrm{Cl}_2)$ = 0.98 mg/l] total chlorine, the relative standard deviation was 1.2 percent. 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 [$\rho(\mathrm{Cl}_2)$ = 0.79 mg/l], the relative standard deviation was 3.3 percent.

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 [$p(\mathrm{Cl}_2)$ = 1.0 and 5.0 mg/l], relative standard deviations of 1.4 percent and 0.88 percent, respectively.

The results presented above 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. It has been found by the quality assurance branch of EMSL-Cincinnati [3] 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.

Table 2- Analytical Parameters from Interlaboratory Analysis for Free Residual Chlorine

(*Clause* 6.8.4)

True Values		Method Code[1]	Number of Laboratories	Mean		Standard Deviation	
$c(\mathrm{Cl_2})$ in µmol/l	$c(\mathrm{Cl_2})$ in 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

[1] A: Iodometric titration amperometric

B : DPD colorimetric

C: DPD titrimetric

7 COLORIMETRIC METHOD USING DPD, FOR ROUTINE CONTROL

7.1 Applicability

This method is appropriate for drinking water and other waters, where additional halogens like bromine, iodine and other oxidizing agents are present in almost negligible amounts. Seawater and waters containing bromides and iodides comprise a group for which special procedures are to be carried out.

This method is applicable to concentrations, in terms of chlorine ($\mathrm{Cl_2}$), from 0.000 4 mmol/l to 0.07 mmol/l (0.03 mg/l to 5 mg/l) total chlorine. For higher concentrations, the test portion is diluted.

Commonly, the method is applied as a field method with mobile photometers and commercially available ready-for-use reagents (liquid reagents, powders and tablets). It is essential that those reagents comply with minimum requirements and contain the essential reagents and a buffer system suitable to adjust the measurement solution to a *p*H range of typically 6.2 to 6.5. If there is doubt that water samples have uncommon *p*H values and/or buffer capacities, the user has to check and, if necessary, to adjust the sample *p*H to the required range. Adjust, if necessary, with sodium hydroxide solution or hydrochloric acid before the test.

In Annex B, a procedure is presented for the determination of free and total chlorine in drinking and other low polluted waters, for disposable planar reagent-filled cuvettes using a mesofluidic channel pump/colorimeter.

7.2 Principle

7.2.1 *Determination of Free Chlorine*

Free chlorine is determined by a direct reaction with *N,N*-dialkyl-1,4-phenylenediamine (DPD) in a *p*H range of 6.2 to 6.5. This leads to the formation of a red colour complex. Measure the colour intensity by photometry, or alternatively, by visual comparison of the colour with a scale of permanent glass, plastics standards or colour card comparators.

If ready-to-use test kits are used, deviant *p*H ranges (buffer systems) may be provided. The user of these test kits has to validate the suitability of the provided buffer systems for the range of sample matrices of interest.

7.2.2 *Determination of Total Chlorine*

The reaction is carried out with DPD in the presence of an excess of potassium iodide. The measurement is then carried out as described in **7.2.1**.

7.3 Interferences

7.3.1 *General*

Manufacturers' instructions on additional interferences shall be considered.

7.3.2 *Interference by Other Chlorine Compounds*

Chlorine dioxide that might be present in the sample in addition to chlorine is measured as total chlorine. This interference may be corrected by specific determination of chlorine dioxide in the water.

If chlorine dioxide is present in the sample as the only disinfectant, it may be measured with the DPD method described in **7.7** with the appropriate conversion factor. Other chlorine compounds do not specifically cause oxidation of DPD.

7.3.3 *lnterference by Compounds Other than Chlorine Compounds*

Depending on the concentration and the chemical oxidation potential, other oxidizing agents affect the reaction, for example, bromine, iodine, bromamines, iodoamines, ozone, hydrogen peroxide, chromate, oxidized manganese, nitrite, iron(III) ions, peracetic acid and copper ions. The interference from Cu(II) (<8 mg/l) and iron (<20 mg/l) is suppressed by the disodium EDTA in reagents **7.4.2** and **7.4.3**.

lnterference by chromate may be eliminated by addition of excess barium chloride.

The user has to validate how to cope with these interferences. In particular, for waste waters or cooling waters, it has to be considered that high amounts of interfering compounds may be present.

NOTE — Bromine and monobromamine contribute to the disinfection effect and regularly occur in chlorine-based disinfection products.

7.3.4 *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 (*see* **7.7.2**) previously treated with the arsenite or thioacetamide solution (*see* **7.4.10**) 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 (*see* **7.4.10**) or thioacetamide solution (*see* **7.4.10**) and mix. Again add 5.0 ml of buffer solution (*see* **7.4.2**) and 5.0 ml of DPD reagent (*see* **7.4.3**) and mix. This procedure to quantify the oxidized manganese interference is given as example. For ready-to-use reagents, other quantities may be required.

Fill the measuring cell with this treated solution and immediately measure the colour under the same conditions as adopted for the calibration. Record c_3, the concentration reading from the comparator scale or calibration graph, corresponding to the oxidized manganese present.

In using comparators with permanent glass colour standards or plastics standards or colour card comparators, the arsenite or thioacetamide treated sample may be used as a blank to compensate for any interference colour so long as the time of addition of reagents is the same for both blank and sample.

7.3.5 *Interference Due to Turbid and Coloured Samples*

If the blank value matching is not possible, then, in case of turbid samples or in the case precipitation occurs due to the addition of the buffer solution, the samples have to be filtered. The filtration equipment and the filter material shall be chlorine demand free. This shall be checked accordingly. (*see* **7.5.3)** for a procedure to prepare the glassware.

Filtration of samples may lead to losses in free chlorine. This can happen although the filters are chlorine demand free. Therefore, the user has to demonstrate that this step does not lead to false results if it cannot be avoided.

7.4 Reagents

During the analysis, use only reagents of recognized analytical grade, and only water as specified in **7.4.1**.

7.4.1 *Water***,** as specified in IS 1070, grade 2, free from oxidizing and reducing substances. Demineralized or distilled water of which the quality is checked as follows.

7.4.1.1 In two 250 ml chlorine-demand-free conical flasks (*see* **7.5.3**) place, in order,

a) In the first: 100 ml of the water to be checked and about 1 g of potassium iodide (*see* **7.4.4**); mix and after 1 min, add 5 ml of buffer solution (*see* **7.4.2**) and 5.0 ml of DPD reagent (*see* **7.4.3**), and
b) In the second: 100 ml of the water to be checked and two drops of sodium hypochlorite solution (*see* **7.4.7**); then, after 2 min, 5.0 ml of buffer solution (*see* **7.4.2**) and 5 ml of DPD reagent (*see* **7.4.3**).

7.4.1.2 No colouration should appear in the first flask whereas it is essential that a light pink colouration appears in the second flask. If the demineralized or distilled water does not have the desired quality, it shall be chlorinated according to the following procedure.

a) First, chlorinate the demineralized or distilled water to a level of about 0.14 mmol/l (10 mg/l) and store it in a well-stoppered carboy for at least 16 h.
b) Then decholorinate the water by exposure to UV irradiation, sunlight for several hours or by contact with active carbon.
c) Finally, check the quality using the procedures as given in **7.7**. The user has to make sure that the glassware is also chlorine demand free. The procedure is described in **7.5.3**.
d) Recheck the quality after a period of contact followed by dechlorination.

The volumes given to check the quality of water are given as example, since for ready-to-use reagents, other quantities could be used.

7.4.2 *Buffer Solution*, *p*H 6.5.

Dissolve in water (*see* **7.4.1**) in this order: 24 g of 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 dihydrogen ethylenedinitrilotetraacetate 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 chlorine test caused by any trace amounts of iodide in the reagents.

Dilute to 1 000 ml and mix. The buffer solution is stable for up to 3 months, if stored in a tightly sealed container in the dark. In reference to guaranteed stability of ready-to-use buffer solutions, see the recommendations of the manufacturer.

The buffer solution is an essential part for a proper reaction of DPD with chlorine. Therefore, this buffer system also applies to the various reagents provided in ready-to-use test kits. Such ready-to-use test kits are commonly intended for a certain range of buffer capacities in the samples. Therefore, the buffer capacity of the test kit may be too low. Therefore, the user should make sure that the *p*H of the final reagent sample mix lies between **6.2** and **6.5**. If test kits use modified buffer systems with a deviant *p*H range, it is up to the user to validate the suitability of this system for the matrices and samples of interest.

To prevent contamination of the sample, *p*H checks may be carried out using a *p*H-meter or non-bleeding *p*H-test strips. If necessary, samples should be adjusted to the correct *p*H range using hydrochloric acid or sodium hydroxide solution. If there is no information on the buffer used or the buffer capacity of the test kit, the manufacturer of the test kit shall not refer to this document.

NOTE — Solutions containing mercury should be treated to recover mercury and then it should be disposed as per disposal policy for solid waste in India. Refer to **12** of IS NO. 5182 : Part 2 : 2001 for treatment of mercury containing solutions.

7.4.3 *N,N-dialkyl-1,4-phenylenediamine sulfate (DPD) solution, 1.1 g/l*

The DPD reagent is commercially available. It is available from numerous sources and the usage is handy especially when tests are carried out with test kits on site. It is essential that commercially available DPD reagents contain suitable amounts of acid and EDTA as well as a suitable DPD concentration. If ready-to-use DPD regents are used, evidence has to be given that the composition is as suitable as the formulation given below. If there is no such information, the manufacturer of the ready-to-use test kit shall not refer to this document.

Alternatively, the DPD reagent can be prepared in the laboratory.

Mix 250 ml water (*see* **7.4.1**), 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.

The following alkyderivates of DPD are available:

a) *N,N*-diethyl-1,4-phenylenediamine sulfate
   $[NH_2\text{-}C_6H_4\text{-}N(C_2H_5)_2 \cdot H_2SO_4]$; and
b) *N,N*-dipropyl-1,4-phenylenediamine sulfate
   $[NH_2\text{-}C_6H_4\text{-}N(C_3H_7)_2 \cdot H_2SO_4]$.

Other salts of DPD like oxalates may be used as well. It is up to the user of this standard to prove the equivalence of the results obtained with modified reagents.

Store the reagent in a dark bottle protected from heat. Renew the solution after 1 month or when it becomes discoloured.

In reference to guaranteed stability of ready-to-use DPD solutions, see the recommendations of the manufacturer.

Information by the manufacturer on the buffer system and its usability for the target applications shall be given. The manufacturer shall give information about the DPD used and shall give information that the supplied system generally meets the performance of this method according to Annex C. Otherwise, the manufacturer of the powder, tablets or ready-to-use test kits shall not refer to this method.

NOTE — Liquid reagents (*See* **7.4.2** and *See* **7.4.3**) can be conveniently replaced by combined reagents commercially available in the form of stable powder or tablets or other ready-to-use kits using DPD.

7.4.4 *Potassium Iodide*, Crystals.

7.4.5 *Sulphuric Acid, $c(H_2SO_4) \approx 1$ mol/l*

Take 800 ml water (*see* **7.4.1**) and add cautiously with continuous stirring 54 ml of sulfuric acid (ρ = 1.84 g/ml). Cool to room temperature and transfer the solution to a 1 000 ml volumetric flask. Make up to the mark with water and mix well. Diluted sulfuric acid, $c(H_2SO_4) \approx 1$ mol/l, is commercially available and may be used as well.

7.4.6 *Sodium Hydroxide, c(NaOH) ≈ 2 mol/l*

Weigh 80 g of sodium hydroxide tablets and add to 800 ml water (*see* **7.4.1**) in a conical flask. Stir continuously until all tablets are dissolved. Wait until the solution has cooled to room temperature and transfer this solution to a 1 000 ml one-mark volumetric flask. Make up to the mark with water and mix well.

Solutions of sodium hydroxide, $c(NaOH) \approx 2$ mol/l, are commercially available and may be used as well.

7.4.7 *Sodium Hypochlorite Solution*, $\rho(Cl_2)$ about 0.1 *g/l*

Prepare by dilution of concentrated commercial sodium hypochlorite solution.

7.4.8 *Potassium Iodate Stock Solution*, $\rho(KIO_3)$ = 1.006 *g/l.*

Dissolve 1.006 g of potassium iodate (KlO_3) in about 250 ml water (*see* **7.4.1**) in a 1 000 ml one-mark volumetric flask. Make up to the mark with water and mix.

NOTE — Potassium permanganate is another option for a check standard. It is up to the user to provide the necessary validation data if permanganate is used instead.

7.4.9 *Potassium Iodate Standard Solution*, $\rho(KIO_3)$ = 10.06 *mg/l*

Take 10 ml of stock solution (*see* **7.4.8**), place in a 1 000 ml one-mark volumetric flask, add about 1 g potassium iodide (*see* **7.4.4**) and make up to the mark with water (*see* **7.4.1**).

Prepare this solution on the day of use.

1 ml of this standard solution contains 10.06 µg of KlO_3.10.06 µg of KlO_3 is equivalent to 0.141 µmol Cl_2.

7.4.10 *Sodium Arsenite Solution*, $\rho(NaAsO_2)$ = 2 g/l; or *thioacetamide solution*, $\rho(CH_3CSNH_2)$ = 2.5 g/l.

7.4.11 *Chlorine Solution*, stabilized chlorine standard solution, commercially available.

7.5 Apparatus

Usual laboratory apparatus and, in particular, photometric or colorimetric equipment respectively, comprising one of the following:

7.5.1 *Comparator*, equipped with a scale of permanent glass or plastics colour standards specially set up for the DPD technique and suitable for concentrations from 0.000 4 mmol/l to 0.07 mmol/l (that is 0.03 mg/l to 5 mg/l) of chlorine.

7.5.2 *Spectrometer*, a photometer, colorimeter or spectrophotometer, with a selector for wavelength variation, suitable for use at 510±20 nm or 550±20 nm and equipped with rectangular or cylindrical cells with an optical path length of 10 mm or greater.

7.5.3 *Chlorine-demand free glassware*, obtained by filling with sodium hypochlorite solution (*see* **7.4.7**) then, after 1 h, rinsing copiously with water (*see* **7.4.1**).

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.

7.6 Sampling

If possible, analyze all samples on site within 5 min after sampling. If samples cannot be analyzed on site, use chlorine-demand-free dark glass bottles for transport and storage. Fill sample bottle completely. Analyze samples immediately after arrival in the lab. It is up to the user of this method to determine the maximum storage time of samples. At all times, avoid bright light, agitation and heat.

If immediate analysis on site is impossible, the time between sampling and analysis shall be added to the test report as well as the reason for delay.

7.7 Procedure

7.7.1 *Test Sample*

Start determination immediately after taking samples. If turbid samples have to be processed, preferably use blank value matching. If unavoidable, filter samples. In this case, it is up to the user to ensure that the filtration equipment and the filter material are chlorine demand free. It is recommended to filter turbid samples on site and to use pressure filtration techniques (for example syringe with single use filter cartridge).

7.7.2 *Test Portions*

Take two test portions, each of 100.0 ml (V_0). If the concentration of total chlorine exceeds 70 µmol/l (5 *mg/l*), it is necessary to take a smaller volume, *V*1, of test sample and to dilute with water (*see* **7.4.1**) to 100.0 ml. For ready-to-use test kits, smaller volumes of test portions can be required. *See* recommendations of the manufacturer.

7.7.3 *Calibration*

Place in a series of 100 ml one-mark volumetric flasks increasing quantities of the potassium iodate standard solution (*see* **7.4.9**) in such a way as to set up a scale extending from $c(Cl_2)$ = 0.423 µmol/l up to 70.5 µmol/l [$\rho(Cl_2)$ = 0.03 mg/l up to 5 *mg/*l using 0.3 ml up to 50 ml of standard solution (*see* **7.4.9**)]. Add 1.0 ml sulfuric acid (*see* **7.4.5**) and after 1 min, 1.0 ml of sodium hydroxide solution (*see* **7.4.6**). Dilute to 100 ml with water (*see* **7.4.1**). Transfer the contents of each flask, without rinsing, into a 250 ml conical flask containing 5 ml buffer solution (*see* **7.4.2**) and 5 ml DPD reagent (*see* **7.4.3**), added less than 1 min prior to the transfer, and mix (*see* NOTE). Then fill the measuring cell successively with each of the prepared standard matching solutions and measure within 2 min one of the following:

a) the colour intensity with the comparator (*see* **7.5.1**); and

b) the absorbance, against water in the reference cell, with a spectrometer (*see* **7.5.2**).

As required, check and make any necessary corrections to the comparator scale of standards or prepare a calibration graph for the spectrometer. Carry out a calibration according to ISO 8466-1 for each fresh preparation of DPD reagent and check daily one point on the scale or on the graph. Depending on the instrument used, a non-linear calibration function can also be appropriate.

Field photometers of ready-to-use test kits are calibrated by the manufacturer. Manufacturers' instructions shall be followed.

NOTE — Prepare each standard matching solution separately to avoid the mixture of buffer and reagent standing too long in advance and the appearance of a false red colour.

7.7.4 *Determination of Free Chlorine*

Transfer the first test portion, without rinsing, to a 250 ml conical flask containing 5 ml of buffer solution (*see* **7.4.2**) and 5 ml of DPD reagent (*see* **7.4.3**) and mix. Fill the measuring cell with this treated solution and immediately measure the colour under the same conditions as adopted for the calibration (*see* **7.7.3**). Record c_1, the concentration reading from the comparator scale or calibration graph (*see* **7.7.3**).

Depending on the instrument or ready-to-use test kit used, other volumes of reagents and vessels may be used according to the manufacturer's recommendations. Furthermore, the reaction time can be adjusted according to the manufacturer's recommendations.

In the case of an unknown water, possibly with a high acidity, a high alkalinity or a high concentration of salts, it is advisable to verify that the volume of buffer solution (*see* **7.4.2**) added is sufficient to bring the water to *p*H 6.2 to 6.5. If not, use a greater volume of the buffer solution (*see* **7.4.2**). In this case, calculate the dilution factor and consider accordingly when calculating the results.

This has to be considered accordingly when ready-to-use test kits are used. Alternatively, if it is in doubt that the *p*H range of 6.2 to 6.5 or a suitably modified range is reached in the final reagent sample mix using powders, tablets or other ready-to-use kits, the *p*H should be measured using appropriate *p*H measuring techniques in the final reagent sample mix. In the case that the *p*H is not reached in the mix, the *p*H of the sample shall be adjusted carefully be adding hydrochloric acid or sodium hydroxide solution. If the sample is significantly diluted (>5 percent to 10 percent) due to *p*H adjustment, this has to be considered accordingly when calculating the result.

7.7.5 *Determination of Total Chlorine*

Transfer the second test portion, without rinsing, to a 250 ml conical flask containing 5 ml of buffer solution (*see* **7.4.2**) and 5 ml of DPD reagent (*see* **7.4.3**), add about 1 g of potassium iodide (*see* **7.4.4**) and mix. Fill the measuring cell with this treated solution and after 2 min, measure the colour under the same conditions as adopted for the calibration (*see* **7.7.3**). Record c_2, the concentration reading from the comparator scale or calibration graph (*see* **7.7.3**).

Depending on the instrument or ready-to-use test kit used, other volumes of reagents, vessels and reaction times may be used according to the recommendation of the manufacturer.

In the case of an unknown water, possibly with a high acidity, a high alkalinity or a high concentration of salts, it is advisable to verify that the volume of buffer solution (*see* **7.4.2**) added is sufficient to bring the water to *p*H 6.2 to 6.5. If not, use a greater volume of the buffer solution (*see* **7.4.2**). In this case, calculate the dilution factor and consider accordingly when calculating the results.

This has to be considered accordingly when ready-to-use test kits are used. Alternatively, if it is in doubt that the *p*H range of 6.2 to 6.5 or a suitably modified range is reached in the final reagent sample mix using powders, tablets or other ready-to-use kits, the *p*H should be measured using appropriate *p*H measuring techniques in the final reagent sample mix. In the case that the *p*H is not reached in the mix, the *p*H of the sample shall be adjusted carefully be adding hydrochloric acid or sodium hydroxide solution. If the sample is significantly diluted (> 5 percent to 10 percent) due to *p*H adjustment, this has to be considered accordingly when calculating the result.

7.8 Calculation

7.8.1 *Calculation of the Free Chlorine Concentration*

The concentration of free chlorine, $c(\mathrm{Cl}_2, \text{free})$, expressed in mmol per litre, is given by the following equation:

$$c(\mathrm{Cl}_{2,\,\text{free}}) = \frac{(c_2 - c_3)V_0}{V_1}$$

where

c_1 = concentration, expressed in mmol of Cl_2 per litre, of chlorine as determined in **7.7.4**;

c_3 = concentration, expressed in mmol of Cl_2 per litre, corresponding to the oxidized manganese present (*see* **7.3.4**);

NOTE — If oxidized manganese is absent, $c_3 = 0$.

V_0 = maximum volume, in ml, of the test portion (*see* **7.7.2**) (V_0 = 100.0 *ml*); and

V_1 = volume, in ml, of test sample in the diluted test portion (*see* **7.7.2**).

7.8.2 *Calculation of the Total Chlorine Concentration*

The concentration of total chlorine, $c(\mathrm{Cl}_2, \text{total})$, expressed in mmol per litre, is given by the following equation:

$$c(\mathrm{Cl}_{2,\ \text{total}}) = \frac{(c_2 - c_3)V_0}{V_1}$$

where

c_2= concentration, expressed in mmol of Cl_2 per litre, of chlorine as determined in **7.7.5**; and

c_3, V_0 and $V_1$are as defined in **7.8.1**.

7.8.3 *Conversion of Amount of Substance Concentration to Mass Concentration*

The chlorine concentration expressed in mmol per litre may be expressed as a mass concentration in mg per litre by multiplying using a conversion factor of 70.91.

7.9 Expression of Results

Results are expressed in mg per litre applying the dilution factors used for each sample. The analysis results obtained when applying this method are subject to a measurement uncertainty that is to be considered in the interpretation of the results.

ANNEX A

(*Clause* 6.1)

(*Informative*)

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* **6.1**).

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; and

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 **6.4** 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 **6.5**.

A- 5 PROCEDURE

A-5.1 Test Sample

See **6.5.1**.

A-5.2 Test Portions

Work on two test portions similar to those in **6.5.2**.

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 (*see* **6.4.2**), 5.0 ml of DPD reagent (*see* **6.4.3**), the third test portion and two drops (about 0.1 ml) of potassium iodide solution (*see* **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(ll) sulfate solution (*see* **6.4.6**). Note the volume, V_6, in ml, 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 (**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 (**6.4.2**) and 5.0 ml of DPD reagent (**6.4.3**) added less than 1 min prior to the transfer. Titrate immediately to a colourless end-point with ammonium iron(ll) sulfate solution (**6.4.6**). Note the volume, V_7, in ml, 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 mmol 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 **6.8**; and

V_6 = volume in ml, of the ammonium iron(ll) sulfate solution (**6.4.6**) 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 mmol 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 **6.8**;

V_6 = defined in **A.6.1.1**; and

V_7 = volume, in ml of the ammonium iron(ll) sulfate solution (**6.4.6**) 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 mmol per litre, is given by the equation:

$$c(\mathrm{Cl}_2) = \frac{2c_3(V_7 - V_6)}{V_0}$$

where

c_3, and V_0 are as defined in **6.8**;

V_6 = defined in **A.6.1.1**; and

V_7 = defined in **A.6.1.2**.

A-6.2 Conversations of Amount of Substance Concentration to Mass Concentration

The chlorine concentration expressed in mmoles per litre may be expressed in mg per litre by multiplying by a conversion factor of 70.91.

ANNEX B

(*Clause* 7.1)

(*Informative*)

DISPOSABLE PLANAR REAGENT-FILLED CUVETTES USING A MESOFLUIDIC CHANNEL PUMP/COLORIMETER

B-1 GENERAL

This annex specifies a procedure for the determination of free chlorine and total chlorine in water, readily applicable to laboratory and field testing. It is based on disposable planar reagent-filled cuvettes. The field of application of this method is similar as that for concentrations of free chlorine and total chlorine.

B-2 PRINCIPLE

B-2.1 Determination of Free Chlorine

Free chlorine is determined by a direct reaction with *N, N*-dialkyl-1,4-phenylenediamine (DPD) with chlorine in a *p*H range of 6.2 to 6.5. This leads to the formation of a red compound. Measure the developed colour intensity from a mesofluidic channel colorimeter.

B-2.2 Determination of Total Chlorine

The reaction is carried out with DPD in the presence of an excess amount of potassium iodide. Measure the developed colour intensity from a mesofluidic channel colorimeter.

B-3 REAGENTS

Reagents used in this method are contained in vendor-prepared pre-filled disposable cuvettes.

B-3.1 Disposable Planar Cuvettes

Disposable planar cuvettes are pre-filled by the vendor with powdered *N,N*-dialkyl-1,4-phenylenediamine (DPD), buffer, potassium iodide, and ascorbic acid.

B-4 APPARATUS

Mesofluidic channel colorimeter comprising the following.

B-4.1 Mesofluidic Pump/Colorimeter, designed for planar DPD reagent-filled cuvettes, suitable for concentrations from 0.12 mg/l to 4.6 mg/l of chlorine. The colorimeter, to be suitable for use at 510 nm, 0.030 ml to 0.050 ml sample volume and an optical path of 10 mm or greater.

B-5 PROCEDURE

B-5.1 Test Sample

Test samples are examined on site without pre-treatment that means suspended solids are not removed prior to analysis. Bath collected samples and samples that require dilution or pre-treatment for mitigation of interferences are collected according to **7.6**.

B-5.2 Calibration Verification and Adjustment

Prepare an aqueous calibration verification standard at 2.0 mg/l from chlorine stock standard. Insert a disposable planar pre-filled reagent cuvette into the mesofluidic pump/colorimeter and analyse the sample. If the measured calibration verification standard result is different from the expected value, perform a slope adjustment to the mesofluidic channel pump/colorimeter and re-verify the calibration standard.

B-5.3 Determination of Free Chlorine

Insert a pre-filled reagent planar cuvette for the determination of free chlorine into the mesofluidic channel pump/colorimeter. Place the exposed end of the cuvette into the sample stream to be measured and start the pump on the colorimeter. Sample will be drawn into the cuvette and mixed with DPD and buffer. The resulting reaction is then analysed and displayed by the mesofluidic colorimeter.

B-5.4 Determination of Total Chlorine

Insert a pre-filled reagent planar cuvette for the determination of total chlorine into the mesofluidic channel pump/colorimeter. Place the exposed end of the cuvette into the sample stream to be measured and start the pump on the colorimeter. Sample will be drawn in to the cuvette and mixed with DPD and buffer. The resulting reaction is then analyzed and displayed by the mesofluidic colorimeter.

B-6 CALCULATION

The concentration of free chlorine or total chlorine is automatically calculated based on the internal calibration of the colorimeter for an undiluted sample and is expressed in mg/l chlorine (Cl_2).

B-7 RESULTS OF A VALIDATION TRIAL

Performance data are shown in Annex C.

ANNEX C

(*Clause* 7.4.3 *and* Annex B)

(*Normative*)

PERFORMANCE DATA

C-1 PERFORMANCE DATA FOR DPD COLORIMETRIC METHOD (7)

A final international interlaboratory trial was performed by IWW Water Centre (Germany) in May 2017. Ten laboratories from Germany and the United States of America took part with 17 test kits in total. The planar cuvettes described in Annex B were applied by two laboratories (one test kit each). All participants met at the organizer's lab and performed the tests at the same time under comparable conditions. The original sample matrices were spiked with a sodium hypochlorite stock solution (free chlorine) directly prior to the tests.

Just for the standard solutions (sample F) and the drinking waters (sample A), recovery rates could be calculated. For all other sample matrices, the assigned value cannot be calculated due to the inevitable chlorine consumption of real water matrices.

A set of 15 samples (matrix-level combinations) was analyzed in drinking water, swimming pool water (standard and saline pool), cooling water and in waste water, respectively. The performance data are summarized in Table C-2 for free chlorine and Table C-3 for total chlorine. Further sample information is given in Table C-1.

Table C-1 Information on Samples for the Final Validation Trial in May 2017

(*Clause* C-1)

Sample Type	Matrix	Concentration Level	*p*H	Alkalinity mmol/l	Conductivity µS/cm
A (DW)	Drinking water (Public Water Supply of Muelheim)	1, 2, 3	7.6	2.37	560
B (SW)	Swimming pool water (standard pool)	1,2 Free and total	7.2	0.39	387
C (SW)	Swimming pool water (saline pool)	1,2 Free and total	6.9	0.21	10 800
D (CW)	Cooling water	1, 2	7.3	0.46	930
E (WW)	Waste water (municipal)	1,2	7.8	2.17	1 020
F (ST)	Standard solution ($KMnO_4$) [8]	1, 2, 3, 4	–	–	–

Table C-2 Performance Data for DPD Colorimetric Method, Free Chlorine

(*Clause* C-1)

Sample Type	l	n	o Percent	X mg/l	$\bar{x}$ mg/l	η Percent	s_R mg/l	$C_{V,R}$ Percent	s_r mg/l	$C_{V,r}$ Percent
A (DW 1)	14	42	0.0	0.05	0.042	84.0	0.015 8	37.5	0.006 6	15.6
A (DW 2)	16	48	5.9	0.20	0.188	94.0	0.021 8	11.6	0.011 1	5.9
A (DW 3)	16	48	5.9	2.00	1.827	91.4	0.053 5	2.9	0.015 7	0.9
B (PW 1)	14	42	12.5	–	0.783	–	0.057 3	7.3	0.013 4	1.7
B (PW 2)	15	45	6.3	–	1.004	–	0.073 6	7.3	0.018 9	1.9
C (PW 1)	16	48	0.0	–	0.443	–	0.052 9	11.9	0.017 9	4.0
C (PW 2)	14	41	14.6	–	0.872	–	0.106 9	12.3	0.011 5	1.3
D (CW 1)	14	42	6.7	–	0.292	–	0.109 6	37.5	0.026 3	9.0
D (CW 2)	16	48	5.9	–	0.403	–	0.074 6	18.5	0.023 5	5.8
E (WW 1)	17	51	0.0	–	0.948	–	0.335 1	35.4	0.057 2	6.0
E (WW 2)	17	49	0.0	–	1.982	–	0.186 1	9.4	0.086 7	4.4
F (St 1)	12	36	0.0	0.05	0.044	88.0	0.012 0	27.2	0.007 2	16.4
F (St 2)	14	42	0.0	0.10	0.089	89.0	0.0172	19.3	0.005 7	6.5
F (St 3)	13	39	7.1	0.50	0.448	89.6	0.049 4	11.0	0.008 4	1.9
F (St 4)	14	42	6.7	1.00	0.923	92.3	0.041 5	4.5	0.022 4	2.4

l number of sets.

n number of analytical results after outlier rejection.

o percentage of outliers.

X assigned value.

$\bar{x}$ overall mean of results (without outliers).

η recovery rate.

s_r reproducibility standard deviation.

$C_{V,r}$ coefficient of variation of reproducibility.

s_r repeatability standard deviation.

$C_{V,r}$ coefficient of variation of repeatability.

NOTE-η: Minimum 84.0 percent; maximum 94.0 percent (data available for standard solution and drinking water only).

$C_{V,R}$: Minimum 2.9 percent; maximum 37.5 percent.

$C_{V,r}$: Minimum 0.9 percent; maximum 16.4 percent.

Table C-3 Performance Data for DPD Colorimetric Method, Total Chlorine

(*Clause* C-1)

Sample Type	l	n	o Percent	X mg/l	$\bar{x}$ mg/l	η Percent	s_R mg/l	$C_{V,R}$ Percent	s_r mg/l	$C_{V,r}$ Percent
B (PW 1)	16	48	0.0	–	0.928	–	0.066 4	7.2	0.015 1	1.6
B (PW 2)	15	45	6.3	–	1.172	–	0.055 6	4.7	0.015 8	1.4
C (PW 1)	15	45	6.3	–	0.673	–	0.107 3	15.9	0.009 5	1.4
C (PW 2)	15	44	8.3	–	1.127	–	0.067 6	6.0	0.010 8	1.0

For explanation of symbols, see Table C-2.

NOTE-$C_{V,R}$: Minimum 4.7 Percent; maximum 15.9 percent.

$C_{V,r}$: Minimum 1.0 percent; maximum 1.6 percent.

C-2 PERFORMANCE DATA FOR THE METHOD DESCRIBED IN ANNEX B

The USA-EPA office of drinking water and ground water evaluated the meso fluidic colorimetry method with the results presented in Table C-4.

Table C.4 Analytical Parameters from Interlaboratory Analysis for Free Chlorine

(*Clause* C-2)

True Value mg/l	**Method Code***	**Number of Laboratories (Observations)**	**Mean** mg/l	**Standard Deviation** mg/l
0.20	A	21	0.21	0.01
	B	21	0.21	0.03
2.00	A	12	1.88	0.01
	B	12	1.94	0.04

*

A: DPD colorimetric method as per ISO 7393-2 : 1985.

B: DPD reagent filled planar cuvette mesofluidic channel colorimetry.

ANNEX D

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ANNEX E

(*Foreword*)

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