INTERNATIONAL STANDARD

**ISO 7393-2**

Second edition
2017-12

# Water quality — Determination of free chlorine and total chlorine —

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

*Qualité de l'eau — Dosage du chlore libre et du chlore total —*

*Partie 2: Méthode colorimétrique à la* N,N-*dialkylphénylène-1,4 diamine destinée aux contrôles de routine*

Reference number
ISO 7393-2:2017(E)

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# Foreword

ISO (the International Organization for Standardization) is a worldwide federation of national standards bodies (ISO member bodies). The work of preparing International Standards is normally carried out through ISO technical committees. Each member body interested in a subject for which a technical committee has been established has the right to be represented on that committee. International organizations, governmental and non-governmental, in liaison with ISO, also take part in the work. ISO collaborates closely with the International Electrotechnical Commission (IEC) on all matters of electrotechnical standardization.

The procedures used to develop this document and those intended for its further maintenance are described in the ISO/IEC Directives, Part 1. In particular the different approval criteria needed for the different types of ISO documents should be noted. This document was drafted in accordance with the editorial rules of the ISO/IEC Directives, Part 2 (see www.iso.org/directives).

Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights. Details of any patent rights identified during the development of the document will be in the Introduction and/or on the ISO list of patent declarations received (see www.iso.org/patents).

Any trade name used in this document is information given for the convenience of users and does not constitute an endorsement.

For an explanation on the voluntary nature of standards, the meaning of ISO specific terms and expressions related to conformity assessment, as well as information about ISO's adherence to the World Trade Organization (WTO) principles in the Technical Barriers to Trade (TBT) see the following URL: www.iso.org/iso/foreword.html.

This document was prepared by Technical Committee ISO/TC 147, *Water quality*, Subcommittee SC 2, *Physical, chemical and biochemical methods*.

This second edition cancels and replaces the first edition (ISO 7393-2:1985), which has been technically revised.

The main changes compared to the previous edition are as follows:

- a new Annex C has been included with the title: Disposable planar reagent-filled cuvettes using a mesofluidic channel pump/colorimeter.

A list of all parts in the ISO 7393 series can be found on the ISO website.

# Water quality — Determination of free chlorine and total chlorine —

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

**WARNING — Persons using this document should be familiar with normal laboratory practice. This document does not purport to address all of the safety problems, if any, associated with its use. It is the responsibility of the user to establish appropriate safety and health practices.**

**IMPORTANT — It is essential that tests conducted in accordance with this document be carried out by suitably qualified staff.**

## 1 Scope

This document specifies a method for the determination of free chlorine and total chlorine in water, readily applicable to lab- and field-testing. It is based on measurement of the absorption, the red DPD colour complex in a photometer or the colour intensity by visual comparison of the colour with a scale of standards that is regularly calibrated.

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 in practice applicable to concentrations, in terms of chlorine ($Cl_2$), from, for example, 0,000 4 mmol/l to 0,07 mmol/l (e.g. 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 pH range of typically 6,2 to 6,5. If there is doubt that water samples have uncommon pH values and/or buffer capacities, the user has to check and, if necessary, to adjust the sample pH to the required range. The pH of the sample is within the range of pH 4 and 8. Adjust, if necessary, with sodium hydroxide solution or sulfuric acid before the test.

A procedure 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 is presented in Annex A. In Annex C, 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.

## 2 Normative references

The following documents are referred to in the text in such a way that some or all of their content constitutes requirements of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

ISO 3696, *Water for analytical laboratory use — Specification and test methods*

ISO 5667-3, *Water quality — Sampling — Part 3: Preservation and handling of water samples*

ISO 8466-1, *Water quality — Calibration and evaluation of analytical methods and estimation of performance characteristics — Part 1: Statistical evaluation of the linear calibration function*

## 3 Terms and definitions

For the purposes of this document, the following terms and definitions apply.

ISO and IEC maintain terminological databases for use in standardization at the following addresses:

— IEC Electropedia: available at http://www.electropedia.org/

— ISO Online browsing platform: available at https://www.iso.org/obp

**3.1**
**free chlorine**
chlorine present in the form of hypochlorous acid, hypochlorite ion or dissolved elemental chlorine

Note 1 to entry: See Table 1.

**3.2**
**combined chlorine**
**bound chlorine**
fraction of *total chlorine* (3.3) present in the form of *chloramines* (3.4) and organic chloramines

Note 1 to entry: See Table 1.

**3.3**
**total chlorine**
chlorine present in the form of *free chlorine* (3.1) and *combined chlorine* (3.2)

Note 1 to entry: See Table 1.

**3.4**
**chloramines**
derivatives of ammonia by substitution of one, two or three hydrogen atoms with chlorine atoms

Note 1 to entry: Derivatives are 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 document.

**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, and chloramines |
| Bound chlorine | Combined chlorine | | Difference of total and free chlorine |

## 4 Principle

### 4.1 Determination of free chlorine

Free chlorine is determined by a direct reaction with *N*,*N*-dialkyl-1,4-phenylenediamine (DPD) in a pH 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 pH 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.

### 4.2 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 4.1.

## 5 Interferences

### 5.1 General

Manufacturers' instructions on additional interferences shall be considered.

### 5.2 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 (see References [3], [5] and [6]).

If chlorine dioxide is present in the sample as the only disinfectant, it may be measured with the DPD method described in Clause 9 with the appropriate conversion factor. Other chlorine compounds do not specifically cause oxidation of DPD.

### 5.3 Interference 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 6.2 and 6.3.

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

Interference 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.

### 5.4 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 9.2) previously treated with the arsenite or thioacetamide solution (6.10) 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 (6.10) or thioacetamide solution (6.10) and mix. Again add 5,0 ml of buffer solution (6.2) and 5,0 ml of DPD reagent (6.3) 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.

### 5.5 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 7.3 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.

## 6 Reagents

During the analysis, use only reagents of recognized analytical grade, and only water as specified in 6.1.

**6.1 Water** as specified in ISO 3696, grade 2, free from oxidizing and reducing substances. Demineralized or distilled water of which the quality is checked as follows.

In two 250 ml chlorine-demand-free conical flasks (7.3) place, in order,

a) in the first: 100 ml of the water to be checked and about 1 g of potassium iodide (6.4); mix and after 1 min, add 5 ml of buffer solution (6.2) and 5,0 ml of DPD reagent (6.3), and

b) in the second: 100 ml of the water to be checked and two drops of sodium hypochlorite solution (6.7); then, after 2 min, 5,0 ml of buffer solution (6.2) and 5 ml of DPD reagent (6.3).

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.

- 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.
- Then decholorinate the water by exposure to UV irradiation, sunlight for several hours or by contact with active carbon.
- Finally, check the quality using the procedures as given in Clause 9. The user has to make sure that the glassware is also chlorine demand free. The procedure is described in 7.3.
- Recheck the quality after a period of contact followed by dechlorination.

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

**6.2 Buffer solution**, pH 6,5.

Dissolve in water (6.1) 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 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 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 pH of the final reagent sample mix lies between 6,2 and 6,5. If test kits use modified buffer systems with a deviant pH 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, pH checks may be carried out using a pH-meter or non-bleeding pH-test strips. If necessary, samples should be adjusted to the correct pH 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.

Solutions containing mercury shall be disposed of safely.

### 6.3 ***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 (6.1), 2 ml sulfuric acid ($\rho$ = 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 [$NH_2$-$C_6H_4$-$N(C_2H_5)_2 \cdot H_2SO_4$];

b) *N,N*-dipropyl-1,4-phenylenediamine sulfate [$NH_2$-$C_6H_4$-$N(C_3H_7)_2 \cdot H_2SO_4$].

Other salts of DPD like oxalates may be used as well. It is up to the user of this document 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 document according to Annex B. Otherwise, the manufacturer of the powder, tablets or ready-to-use test kits shall not refer to this document.

NOTE Liquid reagents (6.2 and 6.3) 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.

### 6.4 **Potassium iodide**, crystals.

### 6.5 **Sulfuric acid**, $c(H_2SO_4) \approx 1$ mol/l.

Take 800 ml water (6.1) and add cautiously with continuous stirring 54 ml of sulfuric acid ($\rho$ = 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.

**6.6 Sodium hydroxide**, $c(NaOH) \approx 2$ mol/l.

Weigh 80 g of sodium hydroxide tablets and add to 800 ml water (6.1) 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.

**6.7 Sodium hypochlorite**, solution, $\rho(Cl_2)$ about 0,1 g/l.

Prepare by dilution of concentrated commercial sodium hypochlorite solution.

**6.8 Potassium iodate**, stock solution, $\rho(KIO_3) = 1{,}006$ g/l.

Dissolve 1,006 g of potassium iodate ($KIO_3$) in about 250 ml water (6.1) 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.

**6.9 Potassium iodate**, standard solution, $\rho(KIO_3) = 10{,}06$ mg/l.

Take 10 ml of stock solution (6.8), place in a 1 000 ml one-mark volumetric flask, add about 1 g potassium iodide (6.4) and make up to the mark with water (6.1).

Prepare this solution on the day of use.

1 ml of this standard solution contains 10,06 µg of $KIO_3$.

10,06 µg of $KIO_3$ is equivalent to 0,141 µmol $Cl_2$.

**6.10 Sodium arsenite**, solution, $\rho(NaAsO_2) = 2$ g/l; or **thioacetamide,** solution, $\rho(CH_3CSNH_2) = 2{,}5$ g/l.

**6.11 Chlorine solution**, stabilized chlorine standard solution, commercially available.

## 7 Apparatus

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

**7.1 Comparator**, equipped with a scale of permanent glass or plastics colour standards specially set up for the DPD technique and suitable for concentrations from, for example, 0,000 4 mmol/l to 0,07 mmol/l (e.g. 0,03 mg/l to 5 mg/l) of chlorine.

**7.2 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.

**7.3 Chlorine-demand free glassware**, obtained by filling with sodium hypochlorite solution (6.7) then, after 1 h, rinsing copiously with water (6.1).

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.

## 8 Sampling

If possible, analyse all samples on site within 5 min after sampling (ISO 5667-3). If samples cannot be analysed on site, use chlorine-demand-free dark glass bottles for transport and storage. Fill sample bottle completely. Analyse samples immediately after arrival in the lab. It is up to the user of this document 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 the lab measurement.

## 9 Procedure

### 9.1 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 (e.g. syringe with single use filter cartridge).

### 9.2 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 (6.1) to 100,0 ml. For ready-to-use test kits, smaller volumes of test portions can be required. See recommendations of the manufacturer.

### 9.3 Calibration

Place in a series of 100 ml one-mark volumetric flasks increasing quantities of the potassium iodate standard solution (6.9) in such a way as to set up a scale extending from $c(\text{Cl}_2)$ = 0,423 µmol/l up to 70,5 µmol/l [$\rho(\text{Cl}_2)$ = 0,03 mg/l up to 5 mg/l; 0,3 ml up to 50 ml of standard solution (6.9)]. Add 1,0 ml sulfuric acid (6.5) and after 1 min, 1,0 ml of sodium hydroxide solution (6.6). Dilute to 100 ml with water (6.1). Transfer the contents of each flask, without rinsing, into a 250 ml conical flask containing 5 ml buffer solution (6.2) and 5 ml DPD reagent (6.3), added less than 1 min prior to the transfer, and mix (see the NOTE). Then fill the measuring cell successively with each of the prepared standard matching solutions and measure within 2 min one of the following:

- the colour intensity with the comparator (7.1);
- the absorbance, against water in the reference cell, with a spectrometer (7.2).

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.

### 9.4 Determination of free chlorine

Transfer the first test portion, without rinsing, to a 250 ml conical flask containing 5 ml of buffer solution (6.2) and 5 ml of DPD reagent (6.3) 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 9.3). Record $c_1$, the concentration reading from the comparator scale or calibration graph (see 9.3).

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 (6.2) added is sufficient to bring the water to pH 6,2 to 6,5. If not, use a greater volume of the buffer solution (6.2). 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 pH 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 pH should be measured using appropriate pH measuring techniques in the final reagent sample mix. In the case that the pH is not reached in the mix, the pH of the sample shall be adjusted carefully be adding hydrochloric acid or sodium hydroxide solution. If the sample is significantly diluted (>5 % to 10 %) due to pH adjustment, this has to be considered accordingly when calculating the result (see Clause 10).

## 9.5 Determination of total chlorine

Transfer the second test portion, without rinsing, to a 250 ml conical flask containing 5 ml of buffer solution (6.2) and 5 ml of DPD reagent (6.3), add about 1 g of potassium iodide (6.4) and mix (see the NOTE to 6.3). 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 9.3). Record $c_2$, the concentration reading from the comparator scale or calibration graph (see 9.3). If the sample is significantly diluted (>5 % to 10 %) due to pH adjustment, this has to be considered accordingly when calculating the result (see Clause 10).

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 or a high alkalinity or with a high concentration of salts, it is advisable to verify that the volume of buffer solution (6.2) added is sufficient to bring the water to pH 6,2 to 6,5. If not, use a greater volume of the buffer solution (6.2).

This has to be considered accordingly when ready-to-use test kits are used. Alternatively, if it is in doubt that the pH 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 pH should be measured using appropriate pH measuring techniques in the final reagent sample mix. In the case that the pH is not reached in the mix, the pH of the sample shall be adjusted carefully be adding hydrochloric acid or sodium hydroxide solution. If the sample is significantly diluted (>5 % to 10 %) due to pH adjustment, this has to be considered accordingly when calculating the result (see Clause 10).

# 10 Calculation

## 10.1 Calculation of the free chlorine concentration

The concentration of free chlorine, $c(\mathrm{Cl}_{2,\,\mathrm{free}})$, expressed in millimoles per litre, is given by Formula (1):

$$c\left(\mathrm{Cl}_{2,\mathrm{free}}\right)=\frac{\left(c_1-c_3\right)V_0}{V_1} \tag{1}$$

where

$c_1$ is the concentration, expressed in millimoles of $\mathrm{Cl}_2$ per litre, of chlorine as determined in 9.4;

$c_3$ is the concentration, expressed in millimoles of $\mathrm{Cl}_2$ per litre, corresponding to the oxidized manganese present (see 5.3);

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

$V_0$ is the maximum volume, in millilitres, of the test portion (6.2) ($V_0$ = 100,0 ml);

$V_1$ is the volume, in millilitres, of test sample in the test portion after dilution (9.2).

## 10.2 Calculation of the total chlorine concentration

The concentration of total chlorine, $c(\mathrm{Cl}_{2,\,\mathrm{total}})$, expressed in millimoles per litre, is given by Formula (2):

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

where

$c_2$ is the concentration, expressed in millimoles of $\mathrm{Cl}_2$ per litre, of chlorine as determined in 9.5;

$c_3$, $V_0$ and $V_1$ are as defined in 10.1.

## 10.3 Conversion of amount of substance concentration to mass concentration

The chlorine concentration expressed in millimoles per litre may be expressed as a mass concentration in milligrams per litre by multiplying using a conversion factor of 70,91.

# 11 Expression of results

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

EXAMPLE

Free chlorine, $\rho(\mathrm{Cl}_{2,\,\mathrm{free}})$ = 0,65 mg/l;

Total chlorine, $\rho(\mathrm{Cl}_{2,\,\mathrm{total}})$ = 2,1 mg/l.

# 12 Test report

The test report shall contain at least the following information:

a) the test method used, together with a reference to this document, i.e. ISO 7393-2;

b) the identity of the sample;

c) expression of the results according to Clause 11;

d) any deviation from this method;

e) report of all circumstances that can have affected the results;

f) time between sampling and analysis as well as the reason for the lab measurement if the measurement was not carried out on site.

# Annex A
(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 Clause 1).

## A.2 Principle

After determination of free chlorine and total chlorine, colorimetric measurement of two further test portions is to be conducted:

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: 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. The concentration of combined chlorine caused by monochloramine and dichloramine types and the concentration of nitrogen trichloride have to be calculated accordingly.

## A.3 Reagents

Use the reagents as given in Clause 6 and in addition:

**A.3.1 Potassium iodide**, solution, $\rho(KIO_2)$ = 5 g/l.

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

## A.4 Apparatus

See Clause 7.

## A.5 Procedure

### A.5.1 Test sample

See 9.1.

### A.5.2 Test portions

Work on two test portions similar to those given in 9.2.

### A.5.3 Calibration

See 9.3.

### A.5.4 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 (6.2), 5,0 ml of DPD reagent (6.3), the third test portion and two drops (approximately 0,1 ml) of potassium iodide solution (A.3.1) or a very small crystal of potassium iodide (approximately 0,5 mg) and mix. Fill the measuring cell with this solution and immediately measure the colour under the same conditions as adopted for the calibration (see A.5.3). Record $c_4$, the concentration reading from the comparator scale or calibration graph (see A.5.3).

### A.5.5 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 (approximately 0,1 ml) of potassium iodide solution (A.3.1) or a very small crystal of potassium iodide (approximately 0,5 mg) and mix. Transfer the contents of the beaker to a 250 ml conical flask containing 5,0 ml of buffer solution (6.2) and 5,0 ml of DPD reagent (6.3) added less than 1 min prior to the transfer. Fill the measuring cell with this solution and immediately measure the colour under the same conditions as adopted for the calibration (see A.5.3). Record $c_5$, the concentration reading from the comparator scale or calibration graph (see A.5.3).

## 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 Formula (A.1):

$$c(\mathrm{Cl}_2)=\frac{(c_4-c_1)V_0}{V_1} \tag{A.1}$$

where

$c_4$ is the concentration, expressed in millimoles of $\mathrm{Cl_2}$ per litre, of chlorine as determined in A.5.4;

$c_1$, $V_0$ and $V_1$ are as defined in 10.1.

#### 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 Formula (A.2):

$$c(\mathrm{Cl}_2)=\frac{(c_2-2c_5+c_4)V_0}{V_1} \tag{A.2}$$

where

| | |
|---|---|
| $c_2$, $V_0$ and $V_1$ | are as defined in 10.1; |
| $c_4$ | is as defined in A.6.1.1; |
| $c_5$ | is the concentration, expressed in millimoles of $Cl_2$ per litre, of chlorine as determined in A.5.5. |

### 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, $c(Cl_2)$, expressed in millimoles per litre, is given by Formula (A.3):

$$c\left(\mathrm{Cl}_2\right)=\frac{2\left(c_5-c_4\right)V_0}{V_1} \tag{A.3}$$

where

| | |
|---|---|
| $c_5$ | is as defined in A.6.1.2; |
| $\mathrm{c}_4$ | is as defined in A.6.1.1; |
| $V_0$ and $V_1$ | are as defined in 10.1. |

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

The chlorine concentration expressed in millimoles per litre may be expressed as mass concentration in milligrams per litre by multiplying by a conversion factor of 70,91.

# Annex B
(informative)

# Performance data

## B.1 Performance data for the method described in the main part of this document

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 C 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 analysed in drinking water, swimming pool water (standard and saline pool), cooling water and in waste water, respectively. The performance data are summarized in Table B.2 for free chlorine and Table B.3 for total chlorine. Further sample information is given in Table B.1.

**Table B.1 — Information on samples for the final validation trial in May 2017**

| Sample type | Matrix | Concentration level | pH | Alkalinity mmol/l | Conductivity µS/cm |
|---|---|---|---|---|---|
| A (DW) | Drinking water<br>(Public Water Supply of Muelheim) | 1, 2, 3 | 7,6 | 2,37 | 560 |
| B (SW) | Swimming pool water (standard pool) | 1,2<br>Free and total | 7,2 | 0,39 | 387 |
| C (SW) | Swimming pool water (saline pool) | 1,2<br>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 ($KMnO_4$) (Reference [10]) | 1, 2, 3, 4 | — | — | — |

### Table B.2 — Performance data for the final validation of this document, free chlorine

| **Sample type** | $l$ | $n$ | $o$<br>% | $X$<br>mg/l | $\bar{\bar{x}}$<br>mg/l | $\eta$<br>% | $s_R$<br>mg/l | $C_{V,R}$<br>% | $s_r$<br>mg/l | $C_{V,r}$<br>% |
|---|---|---|---|---|---|---|---|---|---|---|
| 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 | 0,017 2 | 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.

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

$\eta$ 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 $\eta$: Minimum 84,0 %; maximum 94,0 % (data available for standard solution and drinking water only).
$C_{V,R}$: Minimum 2,9 %; maximum 37,5 %.
$C_{V,r}$: Minimum 0,9 %; maximum 16,4 %.

### Table B.3 — Performance data for the final validation of this document, total chlorine

| **Sample type** | $l$ | $n$ | $o$<br>% | $X$<br>mg/l | $\bar{\bar{x}}$<br>mg/l | $\eta$<br>% | $s_R$<br>mg/l | $C_{V,R}$<br>% | $s_r$<br>mg/l | $C_{V,r}$<br>% |
|---|---|---|---|---|---|---|---|---|---|---|
| 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 B.2.

NOTE $C_{V,R}$: Minimum 4,7 %; maximum 15,9 %.
$C_{V,r}$: Minimum 1,0 %; maximum 1,6 %.