



# SLOVENSKI STANDARD SIST EN ISO 7393-1:2000

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Water quality - Determination of free chlorine and total chlorine - Part 1: Titrimetric method using N, N-diethyl-1,4-phenylenediamine (ISO 7393-1:1985)

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

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

Ta slovenski standard je istoveten z: EN ISO 7393-1:2000

**ICS:**

13.060.50 Examination of water for chemical substances

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EUROPEAN STANDARD

EN ISO 7393-1

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English version

Water quality - Determination of free chlorine and total chlorine -  
Part 1: Titrimetric method using *N,N*-diethyl-1,4-  
phenylenediamine (ISO 7393-1:1985)

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

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

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

CEN members are bound to comply with the CEN/CENELEC Internal Regulations which stipulate the conditions for giving this European Standard the status of a national standard without any alteration. Up-to-date lists and bibliographical references concerning such national standards may be obtained on application to the Central Secretariat or to any CEN member.

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

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EUROPEAN COMMITTEE FOR STANDARDIZATION  
COMITÉ EUROPÉEN DE NORMALISATION  
EUROPÄISCHES KOMITEE FÜR NORMUNG

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

Page 2  
EN ISO 7393-1:2000

## Foreword

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

This European Standard shall be given the status of a national standard, either by publication of an identical text or by endorsement, at the latest by July 2000, and conflicting national standards shall be withdrawn at the latest by July 2000.

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

## Endorsement notice

The text of the International Standard ISO 7393-1:1985 has been approved by CEN as a European Standard without any modification.

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# International Standard



# 7393/1

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

iTeh STANDARD PREVIEW

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

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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.

Draft International Standards adopted by the technical committees are circulated to the member bodies for approval before their acceptance as International Standards by the ISO Council. They are approved in accordance with ISO procedures requiring at least 75 % approval by the member bodies voting.

International Standard ISO 7393/1 was prepared by Technical Committee ISO/TC 147, *Water quality*.

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

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

### 0 Introduction

ISO 7393 consists of the following parts:

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

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

Part 3: Iodometric titration method for the determination of total chlorine.<sup>1)</sup>

### 1 Scope and field of application

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

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

The method is applicable to concentrations, in terms of chlorine ( $\text{Cl}_2$ ), from 0,000 4 to 0,07 mmol/l (0,03 to 5 mg/l) total chlorine and at higher concentrations by dilution of samples. For concentrations above 0,07 mmol/l, ISO 7393/3 can also be used.

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

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

### 2 Definitions (see table 1)

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

**2.1 free chlorine:** Chlorine present in the form of hypochlorous acid, hypochlorite ion or dissolved elemental chlorine.

**2.2 combined chlorine:** The fraction of total chlorine present in the form of chloramines and organic chloramines.

**2.3 total chlorine:** Chlorine present in the form of "free chlorine" or "combined chlorine" or both.

**2.4 chloramines:** Derivatives of ammonia by substitution of one, two or three hydrogen atoms with chlorine atoms (monochloramine  $\text{NH}_2\text{Cl}$ , dichloramine  $\text{NHCl}_2$ , nitrogen trichloride  $\text{NCl}_3$ ) and all chlorinated derivatives of organic nitrogen compounds as determined by the method specified in this part of ISO 7393.

### 3 Principle

#### 3.1 Determination of free chlorine

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

#### 3.2 Determination of total chlorine

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

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

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

1) At present at the stage of draft.

## ISO 7393/1-1985 (E)

## 4 Reagents

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

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

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

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

- in the first: 100 ml of the water to be checked and about 1 g of potassium iodide (4.4); mix and after 1 min add 5 ml buffer solution (4.2) and 5,0 ml of DPD reagent (4.3);
- in the second: 100 ml of the water to be checked and two drops of sodium hypochlorite solution (4.8); then, after 2 min, 5,0 ml of buffer solution (4.2) and 5 ml of DPD reagent (4.3).

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

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

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

## 4.2 Buffer solution, pH 6,5.

Dissolve in water (4.1) in this order: 24 g anhydrous disodium hydrogen phosphate ( $\text{Na}_2\text{HPO}_4$ ) or 60,5 g of the dodecahydrate form ( $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$ ) and 46 g of potassium dihydrogen phosphate ( $\text{KH}_2\text{PO}_4$ ). Add 100 ml of 8 g/l disodium dihydrogenethylenedinitrilotetraacetate dihydrate (disodium EDTA dihydrate,  $\text{C}_{10}\text{H}_{14}\text{N}_2\text{O}_8\text{Na}_2 \cdot 2\text{H}_2\text{O}$ ) solution (or 0,8 g of the solid form).

If necessary, add 0,020 g of mercury(II) chloride ( $\text{HgCl}_2$ ), to prevent mould growth and interference in the free available chlorine test caused by any trace amounts of iodide in the reagents.

Dilute to 1 000 ml and mix.

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

4.3 *N,N*-diethyl-1,4-phenylenediamine sulfate (DPD)  $[\text{NH}_2\text{-C}_6\text{H}_4\text{-N}(\text{C}_2\text{H}_5)_2 \cdot \text{H}_2\text{SO}_4]$ , solution, 1,1 g/l.

Mix 250 ml water (4.1), 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.

Store the reagent in a dark bottle protected from heat.

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

## 4.4 Potassium iodide, crystals.

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

4.5 Ammonium iron(II) sulfate, stock solution,  $c[(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}] = 0,056$  mol/l.

## 4.5.1 Preparation of the solution

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

Store in a dark bottle.

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

## 4.5.2 Standardization of the solution

Place in a 250 ml conical flask, 50,0 ml of the stock solution (4.5.1), about 50 ml water (4.1), 5 ml orthophosphoric acid ( $\rho = 1,71$  g/ml) and 4 drops of barium diphenylamine sulfonate indicator (4.9). Titrate with potassium dichromate solution (4.10). The end-point is reached when one drop produces an intense purple coloration which remains unchanged after further addition of the potassium dichromate solution. The concentration,  $c_1$ , expressed in millimoles of  $\text{Cl}_2$  per litre, of this solution is given by the equation

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

where

$c_2$  is the concentration of the potassium dichromate standard reference solution (4.10),  
 $c(1/6 \text{ K}_2\text{Cr}_2\text{O}_7) = 100$  mmol/l;

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

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

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

4.6 Ammonium iron(II) sulfate, standard volumetric solution,  $c[(\text{NH}_4)_2\text{Fe}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}] = 2,8$  mmol/l.

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



Transfer to a dark bottle.

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

The concentration,  $c_3$ , expressed in millimoles of  $\text{Cl}_2$  per litre, of this solution is given by the equation

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

where  $c_1$  is as defined in 4.5.2.

**4.7 Sodium arsenite** ( $\text{NaAsO}_2$ ), solution, 2 g/l; or **thioacetamide** ( $\text{CH}_3\text{CSNH}_2$ ), solution, 2,5 g/l.

**4.8 Sodium hypochlorite**, solution [ $\rho(\text{Cl}_2)$  about 0,1 g/l].

Prepare by dilution of concentrated commercial sodium hypochlorite solution.

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

Dissolve 0,3 g barium diphenylamine sulfonate [ $(\text{C}_6\text{H}_5\text{-NH-C}_6\text{H}_4\text{-SO}_3)_2\text{Ba}$ ] in 100 ml water.

**4.10 Potassium dichromate**, standard reference solution,  $c(1/6 \text{ K}_2\text{Cr}_2\text{O}_7) = 100 \text{ mmol/l}$ .

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

## 5 Apparatus

Ordinary laboratory apparatus, and

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

### NOTE ON THE PREPARATION OF GLASSWARE

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

## 6 Procedure

### 6.1 Test sample

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

### 6.2 Test portions

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

### 6.3 Determination of free chlorine

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

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

### 6.4 Determination of total chlorine

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

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

## 7 Correction of interference due to the presence of oxidized manganese

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

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

## 8 Expression of results

### 8.1 Method of calculation

#### 8.1.1 Calculation of the free chlorine concentration

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