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Water quality — Determination of free chlorine and total chlorine —

Part 3:

Iodometric titration method for the determination of
total chlorine

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

Partie 3: Méthode par titrage iodométrique pour le dosage du chlore total



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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 7393-3 was prepared by Technical Committee ISO/TC 147, *Water quality*.

This second edition cancels and replaces the first edition (ISO 7393-3: 1986), of which it constitutes a minor revision.

ISO 7393 consists of the following parts, under the general title *Water quality — Determination of free chlorine and total chlorine*:

- *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*

Annex A forms an integral part of this part of ISO 7393. Annexes B and C are for information only.

Water quality — Determination of free chlorine and total chlorine —

Part 3:

Iodometric titration method for the determination of total chlorine

1 Scope

This part of ISO 7393 specifies an iodometric titration method for the determination of total chlorine in water.

The method is applicable for the measurement of concentrations in terms of chlorine (Cl_2), from 0,01 mmol/l to 0,21 mmol/l (0,71 mg/l to 15 mg/l).

Several substances interfere in the determination (see clause 10).

In annex B a method for direct titration is specified. This is usually applied to the determination of chlorine concentrations above 7 $\mu\text{mol/l}$ (0,5 mg/l) in treated drinking water.

2 Normative references

The following standards contain provisions which, through reference in this text, constitute provisions of this part of ISO 7393. At the time of publication, the editions indicated were valid. All standards are subject to revision, and parties to agreements based on this part of ISO 7393 are encouraged to investigate the possibility of applying the most recent editions of the standards indicated below. Members of IEC and ISO maintain registers of currently valid International Standards.

ISO 5667-1 : 1980, *Water quality — Sampling — Part 1: Guidance on the design of sampling programmes*.

ISO 5667-2 : 1982, *Water quality — Sampling — Part 2: Guidance on sampling techniques*.

3 Definitions (see table 1)

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

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 present in the form of chloramines and organic chloramines.

3.3 total chlorine: Chlorine present in the form of "free chlorine" or "combined chlorine" 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 , and nitrogen trichloride NCl_3) and all chlorinated derivatives of organic nitrogen compounds.

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

4 Principle

Reaction in acid solution of total chlorine and potassium iodide with liberation of free iodine. Instantaneous reduction of the iodine by a known excess of thiosulfate standard solution previously added to the solution. Titration of the unreacted thiosulfate with potassium iodate standard reference solution.

5 Reagents

During the analysis, use only reagents of recognized analytical grade, and water as specified in 5.1.

5.1 Water, free from chlorine and reducing substances.

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

Into two 250 ml chlorine-demand free conical flasks (see clause 6) place, in order,

a) in the first: 100 ml of the water to be checked, and about 1 g of potassium iodide (5.2), 2 ml of phosphoric acid (5.3) and 1 ml of starch solution (5.6);

b) in the second: 100 ml of the water to be checked, about 1 g of potassium iodide (5.2), 2 ml of phosphoric acid (5.3) and 1 ml of starch solution (5.6). Add 10 drops of 0,1 g/l sodium hypochlorite solution (obtained by dilution of commercial concentrated sodium hypochlorite solution, of which the concentration is determined iodometrically).

No coloration shall appear in the first flask when the water is free from chlorine. In the second flask a light blue colour shall appear.

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 final quality has to be re-checked.

A procedure for chlorination followed by dechlorination is given in annex A.

5.2 Potassium iodide (KI) crystals.

5.3 Phosphoric acid, solution, $c(\text{H}_3\text{PO}_4) \approx 0,87 \text{ mol/l}$.

Dissolve 64 ml of phosphoric acid ($\rho = 1,69 \text{ g/ml}$) in water, cool and dilute to 1 000 ml.

5.4 Potassium iodate, standard reference solution, $c(1/6 \text{ KIO}_3) = 10 \text{ mmol/l}$.

Weigh, to the nearest milligram, 0,360 g of dry potassium iodate. Dissolve in water in a 1 000 ml one-mark volumetric flask, make up to the mark with water and mix.

5.5 Sodium thiosulfate, standard volumetric solution, $c(\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}) \approx 10 \text{ mmol/l}$.

5.5.1 Preparation

Dissolve about 2,48 g of sodium thiosulfate in about 250 ml of water in a 1 000 ml one-mark volumetric flask. Make up to the mark with water and mix.

5.5.2 Standardization

Standardize the solution daily, or immediately prior to use, as follows.

Place 200 ml of water (5.1) in a 500 ml conical flask. Add about 1 g of potassium iodide (5.2) and then introduce, by means of a pipette, 10,0 ml of sodium thiosulfate solution (5.5.1) for stan-

dardization, 2 ml of phosphoric acid (5.3) and 1 ml of starch solution (5.6). Titrate immediately with the potassium iodate standard reference solution (5.4) until the appearance of a blue coloration persisting for at least 30 s occurs. Note the volume of iodate consumed.

The actual concentration, c_1 , expressed in millimoles per litre, of the sodium thiosulfate solution is given by the equation

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

where

c_2 is the concentration, expressed in millimoles per litre, of the potassium iodate standard reference solution [$c(1/6 \text{ KIO}_3) = 10 \text{ mmol/l}$];

V_1 is the volume, in millilitres, of sodium thiosulfate solution (5.5.1) used for the standardization ($V_1 = 10 \text{ ml}$);

V_2 is the volume, in millilitres, of potassium iodate standard reference solution used in the titration.

5.6 Starch, 5 g/l solution, or similar commercial indicator.

6 Apparatus

Usual laboratory equipment and

Burette, with fine tip, permitting the delivery of about 30 drops/ml, measuring up to 25 ml, graduated in divisions of 0,05 ml.

NOTE ON PREPARATION OF GLASSWARE

Chlorine-demand free glassware is obtained by filling with 0,1 g/l sodium hypochlorite then, after 1 h, rinsing thoroughly with distilled water and with water free from chlorine-demand.

7 Sampling and samples

See ISO 5667-1 and ISO 5667-2.

8 Procedure

8.1 Test portion

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

Take a test portion of volume not greater than 200 ml and containing not more than 0,21 mmol/l (15 mg/l) of total chlorine. If the amount of total chlorine is expected to exceed this concentration, dilute the sample with water (5.1) and take a test portion of a volume not exceeding 200 ml.

8.2 Determination

Place the test portion (8.1) in a 500 ml conical flask. Add, in order, about 1 g of potassium iodide (5.2), 2 ml of phosphoric

acid (5.3) and, by means of a pipette, 10,0 ml (V_4) of sodium thiosulphate standard volumetric solution (5.5) followed by 1 ml of starch solution (5.6).

CAUTION — The order in which the reagents are added shall be strictly obeyed, otherwise non-stoichiometric conversion of hypochlorite with thiosulfate may take place.

Titrate immediately with the potassium iodate standard reference solution (5.4) until the appearance of a blue coloration persisting for at least 30 s occurs. Note the volume of potassium iodate consumed (V_3).

9 Expression of results

9.1 Calculation

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

$$c(\text{Cl}_2) = \frac{V_4 c_1 - V_3 c_2}{2 V_0}$$

where

c_1 is the actual concentration, expressed in millimoles per litre, of the sodium thiosulfate standard volumetric solution (5.5);

c_2 is defined in 5.5.2;

V_0 is the volume, in millilitres, before dilution (if any) of the test portion (8.1);

V_3 is the volume, in millilitres, of the potassium iodate standard reference solution (5.4) used in the titration (8.2);

V_4 is the volume, in millilitres, of sodium thiosulfate standard volumetric solution (5.5) used in the titration according to 8.2 ($V_4 = 10$ ml).

The amount-of-substance concentration may be converted to the mass concentration, $\rho(\text{Cl}_2)$, expressed in milligrams per litre, by means of the equation

$$\rho(\text{Cl}_2) = M c(\text{Cl}_2)$$

where M is the molar mass, expressed in grams per mole, of chlorine ($M = 70,91$ g/mol).

9.2 Repeatability and reproducibility

In the following, only figures from the direct titration method are presented.

The USA-EPA Environmental Monitoring and Support Laboratory^[1] evaluated the direct iodometric titration method using phenylarsine oxide as the standard reducing agent in place of sodium thiosulfate.

For distilled water samples at concentrations of $c(\text{Cl}_2) = 3,5$ $\mu\text{mol/l}$ and $56,7$ $\mu\text{mol/l}$ [$\rho(\text{Cl}_2) = 0,25$ mg/l and

$4,02$ mg/l] total chlorine, the relative standard deviations were 0,23 % and 0,76 % respectively. Using drinking water at a concentration of $c(\text{Cl}_2) = 9,6$ $\mu\text{mol/l}$ [$\rho(\text{Cl}_2) = 0,68$ mg/l] total chlorine, the relative standard deviation was 5,2 %. With polluted waters poorer precision was obtained. Taking for example the case of river water at a concentration of $c(\text{Cl}_2) = 4,2$ $\mu\text{mol/l}$ [$\rho(\text{Cl}_2) = 0,30$ mg/l] total chlorine the relative standard deviation was 9,7 %.

Results from direct titrations published by the Department of the Environment^[2] are based upon data obtained using potassium iodate standard reference solution equivalent to the stated chlorine concentrations. These data showed for an equivalent total chlorine concentration of $c(\text{Cl}_2) = 28,2$ $\mu\text{mol/l}$ [$\rho(\text{Cl}_2) = 2$ mg/l], relative standard deviations of 2,2 % to 3,7 % and for $c(\text{Cl}_2) = 282$ $\mu\text{mol/l}$ [$\rho(\text{Cl}_2) = 20$ mg/l], relative standard deviations of 0,39 % to 0,65 %.

The results presented above relate to replicate determinations in the same laboratory and thus provide a measure of the repeatability of the method. In all cases the direct titration procedure was used (see annex B). Attempts in the past to quantify the reproducibility of the method by distribution of samples to different laboratories produced unreliable results because of a general instability of solutions containing free and combined chlorine. More recently the Quality Assurance Branch of EMSL-Cincinnati^[4] discovered 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 analytical parameters for methods in current use as shown in table 2.

10 Interferences

Oxidation of iodide to iodine is not caused specifically by chlorine. Depending on the concentration and the chemical potential, the oxidation is effected by all oxidizing agents. Therefore the method is only applicable in the absence of other oxidizing substances, in particular bromine, iodine, bromoamines, iodoamines, ozone, hydrogen peroxide, permanganate, iodate, bromate, chromate, chlorine dioxide, chlorite, oxidized manganate, nitrite, iron(III) ions, copper(II) ions and manganese(III) ions.

11 Test report

The test report shall include the following information:

- a reference to this part of ISO 7393;
- all information necessary for the complete identification of the sample;
- the results and the method of expression used;
- details of any operations not included in this part of ISO 7393 or regarded as optional, together with any circumstances that may have affected the results.

Table 2 — Analytical parameters from interlaboratory analysis for free chlorine

True value		Method code ¹⁾	Number of laboratories (observations)	Mean		Standard deviation	
$c(\text{Cl}_2)$	$\rho(\text{Cl}_2)$			$\mu\text{mol/l}$	mg/l	$\mu\text{mol/l}$	mg/l
7	0,50	A	3	9,2	0,65	5,1	0,36
		B	6	6,2	0,44	1,3	0,09
		C	7	6,8	0,48	1,8	0,13
		D	2	6,2	0,44	2,7	0,19
11,3	0,80	A	4	11,8	0,84	1,4	0,10
		B	10	10,9	0,77	1,1	0,08
		C	14	11,1	0,79	4,1	0,29
		D	6	11,6	0,82	1,3	0,09
15,5	1,10	A	4	15,9	1,13	1,6	0,11
		B	10	15,5	1,10	2,0	0,14
		C	14	16,2	1,15	5,5	0,39
		D	6	16,5	1,17	1,1	0,08
18,2	1,29	A	4	18,8	1,33	10,2	0,72
		B	6	18,6	1,32	1,3	0,09
		C	7	19,9	1,41	5,4	0,38
		D	2	20,0	1,42	0,6	0,04

1) A: starch-iodine end-point
B: iodometric titration amperometric
C: DPD colorimetric
D: DPD titrimetric

Annex A **(normative)**

Preparation of chlorine-demand free water

To obtain dilution water of the desired quality, demineralized or distilled water is first chlorinated to a level of about 10 mg/l and stored in a well-stoppered carboy for at least 16 h. The water is

then dechlorinated by exposure to UV irradiation for at least half an hour or to direct sunlight for several hours. Finally check the quality using the procedure specified in 5.1.

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Annex B (informative)

Direct iodometric titration procedure for the determination of total chlorine in waters with low organic substances content

B.1 Scope

This annex specifies a method for direct iodometric titration as usually applied to the measurement of total chlorine in treated drinking water. For a test solution with a volume of 500 ml, the lower limit of the range of application is 7 µmol/l (0,5 mg/l). For interferences see clause 10.

B.2 Principle

Oxidation, in acid solution, of potassium iodide by the free and combined chlorine with liberation of iodine which is reduced by titration with standard volumetric sodium thiosulfate solution.

B.3 Reagents

See clause 5.

B.4 Apparatus

See clause 6.

B.5 Procedure

B.5.1 Test portion

Take the precautions given in 8.1.

For concentrations less than 0,014 mmol/l (1 mg/l), take 1 000 ml; for concentrations between 0,014 mmol/l and 0,14 mmol/l (1 and 10 mg/l) take 500 ml, and for higher concentrations take proportionately less. Note the volume taken.

B.5.2 Determination

Place the test portion (B.5.1) in a conical flask or white porcelain dish. Add 2 ml of phosphoric acid (5.3), to reduce the pH to between 2 and 3, and about 1 g of potassium iodide (5.2). Mix and titrate against sodium thiosulfate standard volumetric solution (5.5) until the yellow colour is almost discharged. Then add 1 ml of starch solution (5.6). Continue titration until the blue colour is discharged. Note the volume of thiosulfate solution consumed (V_5).

B.6 Expression of results

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

$$c(\text{Cl}_2) = \frac{c_1 V_5}{2 V_0}$$

where

c_1 is the actual concentration, expressed in millimoles per litre, of the sodium thiosulfate standard volumetric solution (5.5);

V_0 is the volume, in millilitres, of the test portion (B.5.1);

V_5 is the volume, in millilitres, of sodium thiosulfate standard volumetric solution (5.5) used in the titration according to B.5.2.

The amount-of-substance concentration may be converted to the mass concentration, $\rho(\text{Cl}_2)$, expressed in milligrams per litre, by means of the equation

$$\rho(\text{Cl}_2) = M c(\text{Cl}_2)$$

where M is the molecular mass, expressed in grams per mole, of chlorine ($M = 70,91 \text{ g/mol}$).

Annex C (informative)

Bibliography

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