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Water quality — Determination of dissolved anions by liquid chromatography of ions —

Part 4:

Determination of chlorate, chloride and chlorite in water with low contamination

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*Qualité de l'eau — Dosage des anions dissous par chromatographie
des ions en phase liquide —*

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*Partie 4: Dosage des ions chlorate, chlorure et chlorite dans des eaux
faiblement contaminées*

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Contents

	Page
Foreword.....	iv
1 Scope	1
2 Normative references	1
3 Terms and definitions	1
4 Interferences	2
5 Principle	2
6 Reagents	3
7 Apparatus	5
8 Quality requirements for the separator column	6
9 Sampling and sample pre-treatment	8
9.1 General requirements.....	8
9.2 Sample pre-treatment in the case of elevated levels of chloride and bromide.....	9
10 Procedure	9
10.1 Calibration.....	9
10.2 Measurement of samples using the standard calibration procedure.....	10
10.3 Validity check of the calibration function.....	10
11 Calculation	10
12 Expression of results	11
13 Test report	11
Annex A (informative) Performance data	12
Bibliography	15

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).

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This document was prepared by Technical Committee ISO/TC 147, *Water quality*, Subcommittee SC 2, *Physical, chemical and biochemical methods*, in collaboration with the European Committee for Standardization (CEN) Technical Committee CEN/TC 230, *Water analysis*, in accordance with the Agreement on technical cooperation between ISO and CEN (Vienna Agreement).

This second edition cancels and replaces the first edition (ISO 10304-4:1997), which has been technically revised. The main changes compared to the previous edition are as follows:

- Introduction: Deletion of all requirements concerning the application of the method and moving of all of the wording needed to other clauses.
- [Clause 2](#): Deletion of all references made but withdrawn since the publication of the 1997 edition (e.g. ISO 10304-2). All references made to the ISO 5667 series have been moved to Bibliography.
- [Subclause 6.8](#): Various eluent formulations have been reduced to one example.
- [Clause 8](#): The calculation procedure for the peak resolution according to the USP definition [[Formula \(1\)](#)] has been completed with the EP definition [[Formula \(2\)](#)]. Both calculations are equivalent.
- [Subclause 9.1](#): Information that drinking water disinfection treatment using chlorine dioxide can cause the formation of chlorite and chlorate (paragraph 2) and helpful precautions to minimize/eliminate such formation (paragraph 3) have been added.
- [Clause 11](#): The option to report result concentrations in microgram per litre has been added.

A list of all parts in the ISO 10304 series can be found on the ISO website.

Any feedback or questions on this document should be directed to the user's national standards body. A complete listing of these bodies can be found at www.iso.org/members.html.

Water quality — Determination of dissolved anions by liquid chromatography of ions —

Part 4:

Determination of chlorate, chloride and chlorite in water with low contamination

1 Scope

This document specifies a method for the determination of the dissolved anions chlorate, chloride, and chlorite in water with low contamination (e.g. drinking water, raw water or swimming pool water).

The diversity of the appropriate and suitable assemblies and the procedural steps depending on them permit a general description only.

For further information on the analytical technique see Reference [7].

An appropriate pre-treatment of the sample (e.g. dilution) and the use of a conductivity detector (CD), UV detector (UV) or amperometric detector (AD) make the working ranges given in Table 1 feasible.

Table 1 — Working ranges of the analytical method

Anion	Working range mg/l ^a	Detection
Chlorate	0,03 to 10	CD
Chloride	0,1 to 50	CD
Chlorite ^b	0,05 to 1	CD
	0,1 to 1	UV; $\lambda = 207 \text{ nm to } 220 \text{ nm}$
	0,01 to 1	AD; 0,4 to 1,0 V

^a The working range is restricted by the ion-exchange capacity of the columns. If necessary, samples can be adjusted to this range by dilution.

^b The minimum working range for chlorite of 0,05 mg/l was obtained using calibration checks, but the round robin trials (see Table A.4) showed that it is difficult to obtain this with sufficient accuracy, and only if taking great care.

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 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

No terms and definitions are listed in this document.

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

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

— IEC Electropedia: available at <https://www.electropedia.org/>

4 Interferences

Organic acids such as mono- and dicarboxylic acids or disinfection byproducts (e.g. chloroacetic acid) can interfere.

Dissolved organics can react with the working electrode of the amperometric detector, causing a decrease in sensitivity.

The presence of fluoride, carbonate, nitrite and nitrate can cause interference with the determination of chlorate, chloride and chlorite. The respective concentrations given in [Table 2](#) are typical for conductivity, UV and amperometric detectors.

Elevated loads of chloride and bromide can cause interference with the determination of chlorite and chlorate. Remove chloride and bromide with the aid of special exchangers ([9.2](#)).

Solid particles and organic compounds (such as mineral oils, detergents, and humic acids) shorten the lifetime of the separator column. They are therefore eliminated from the sample prior to analysis ([Clause 9](#)).

Table 2 — Typical cross-sensitivity of anions

Relation of the mass concentration ^a of measured ion/interfering ion	Detection method
1 part chlorate / 50 parts bromide	CD
1 part chlorate / 500 parts nitrate	CD
1 part chloride / 500 parts fluoride	CD
1 part chloride / 1 000 parts chlorite	CD
1 part chloride / 50 parts nitrite	CD
1 part chlorite / 100 parts fluoride	CD
1 part chlorite / 10 parts fluoride	UV
1 part chlorite / 1 000 parts carbonate	CD
1 part chlorite / 1 000 parts chloride	CD / UV / AD
1 part chlorite / 100 parts nitrite	AD

^a In case the quality requirements in [Clause 8](#) (e.g. see [Figures 2](#) and [3](#)) are not achieved, the sample shall be diluted.

5 Principle

Liquid chromatographic separation of chlorate, chloride, and chlorite is carried out by means of a separator column. A low-capacity anion exchanger is used as the stationary phase, and usually aqueous solutions of salts of weak mono- and dibasic acids as mobile phases (eluent, [6.8](#)).

Detection is by conductivity (CD) with or without suppressor device, UV or amperometric detector (AD).

When using conductivity detectors it is essential that the eluents have a sufficiently low conductivity. For this reason, conductivity detectors are often combined with a suppressor device (cation exchangers) which will reduce the conductivity of the eluent and transform the sample species into their respective acids.

UV detection measures the absorption directly or indirectly.

Amperometric detection of chlorite is carried out via measurement of the current generated by the oxidation of chlorite. The oxidation voltage for chlorite depends on the pH of the eluent. The use of carbon electrodes has proved successful.

The concentration of the respective anions is determined by a calibration of the overall procedure. Particular cases may require calibration by means of standard addition (spiking). Control experiments are necessary to check the validity of the calibration function. Replicate determinations can be necessary.

6 Reagents

Use only reagents of recognized analytical grade. Carry out weighing with an accuracy of 1 % of the nominal mass. An increase in electrical conductivity due to an uptake of carbon dioxide does not interfere with the determination. Use and prepare alternative concentrations or volumes of solutions as described below, if necessary. Alternatively, use commercially available solutions of the required specification.

6.1 Water.

The water used shall have a resistivity $\geq 18 \text{ M}\Omega \cdot \text{cm}$ (25 °C) and shall not contain particulate matter of a particle size $> 0,45 \mu\text{m}$.

6.2 Sodium hydrogencarbonate, NaHCO_3 .

6.3 Sodium carbonate, Na_2CO_3 .

6.4 Sodium hydroxide solution, $c(\text{NaOH}) = 0,1 \text{ mol/l}$.

6.5 Sodium chlorite, NaClO_2 (80 %).

6.6 Sodium chloride, NaCl .

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6.7 Sodium chlorate, NaClO_3 .

[920dfbae8cc5/iso-fdis-10304-4](https://standards.iteh.ai/catalog/standards/sist/9dcd042a-73c3-4bcb-9083-920dfbae8cc5/iso-fdis-10304-4)

6.8 Eluents.

Degas all eluents used. Take steps to avoid any renewed air pick up during operation (e.g. by helium sparging, inline degasser).

The choice of eluent (e.g. based on sodium carbonate or sodium hydroxide solutions, potassium hydroxide, mixed with organic modifiers, if needed) depends on the choice of column and detector; seek advice from the column supplier. Apply eluents that were prepared: manually, by inline dilution or electrochemically *in situ*. The chosen combination of separator column and eluent shall conform to the resolution requirements stated in 7.1. Use eluents as long as the requirement in [Clause 8](#) is met.

An example for an appropriate eluent manually prepared is given in [6.8.2](#).

6.8.1 Sodium carbonate/sodium hydrogencarbonate concentrate.

For the eluent concentrate preparation:

- Place 19,1 g of sodium carbonate ([6.3](#)) and 14,3 g of sodium hydrogencarbonate ([6.2](#)) into a volumetric flask of nominal capacity 1 000 ml, dissolve in water ([6.1](#)) and dilute to volume with water ([6.1](#)).
- The solution contains 0,18 mol/l of sodium carbonate and 0,17 mol/l of sodium hydrogencarbonate. This solution is stable for several months if stored at 2 °C to 6 °C.

6.8.2 Sodium carbonate/sodium hydrogencarbonate eluent.

The following eluent is applicable for the determination of chlorate, chloride and chlorite:

- Pipette 50 ml of the sodium carbonate/sodium hydrogencarbonate concentrate (6.8.1) into a volumetric flask of nominal capacity 5 000 ml and dilute to volume with water (6.1).
- The solution contains 0,001 8 mol/l of sodium carbonate and 0,001 7 mol/l of sodium hydrogencarbonate. Store the solution in amber-coloured glass and renew it every 3 d.

6.9 Stock solutions.

Prepare stock solutions of concentration $\rho = 1\ 000$ mg/l for each of the anions chlorate, chloride and chlorite.

Dissolve the appropriate mass of each of the substances (6.5, 6.6, 6.7), prepared as stated in Table 3, in approximately 800 ml of water (6.1, degassed with nitrogen or helium), in volumetric flasks of nominal capacity 1 000 ml, add 1 ml of sodium hydroxide solution (6.4). Dilute the volume with water (6.1). The solutions are stable as indicated in Table 3.

Alternatively, use commercially available stock solutions of the required concentration.

Table 3 — Mass of portion, pre-treatment and storage suggestions for stock solutions

Anion	Compound	Concentration derived from substance-portion g/l	Pre-treatment	Storage
Chlorate	NaClO ₃	1,275 3 ± 0,013	Dry in a desiccator only	In glass for one month if kept at 2 °C to 6 °C
Chloride	NaCl	1,648 4 ± 0,017	Dry at 105 °C	In polyethylene for three months if kept at 2 °C to 6 °C
Chlorite ^a	NaClO ₂	approx. 1,7	Dry in a desiccator only	In glass for one week if kept at 2 °C to 6 °C in the dark

^a The concentration of the chlorite stock solution shall be determined iodometrically before use (see ISO 10530:1992, Annex A).

6.10 Standard solutions.

Depending upon the concentrations expected, prepare standard solutions of different anion composition and concentration from the stock solutions (6.9). The risk of changes in concentration caused by interaction with the flask material increases with decreasing anion concentration. Store the standard solutions in polyethylene (PE) flasks. Take into account that sodium chlorite salt can contain up to 20 % sodium chloride. Prepare chlorite standard solutions as described in 6.10.2 to avoid chloride contamination, for example, of the mixed standard solution (6.10.1).

6.10.1 Mixed standard solution of chlorate and chloride.

The mass concentrations of this solution are as follows:

$$\rho_{\text{ClO}_3^-, \text{Cl}^-} = 10 \text{ mg/l}$$

Pipette 1 ml of each of the chlorate and chloride stock solutions (6.9) into a volumetric flask of nominal capacity 100 ml, add 0,1 ml of sodium hydroxide solution (6.4) and fill up to volume with water (6.1).

Prepare the solution on the day of use.

Other mixed standard solutions can be made by respective dilutions of the mixed standard solution.

6.10.2 Chlorite standard solution.

The mass concentration of this solution is as follows:

$$\rho_{\text{ClO}_2^-} = 10 \text{ mg/l}$$

Pipette 1 ml of chlorite stock solution (6.9) into a volumetric flask of nominal capacity 100 ml, add 0,1 ml of sodium hydroxide solution (6.4) and make up to volume with water (6.1).

Prepare the solution on the day of use.

Other standard solutions can be made by respective dilutions of the chlorite standard solution.

6.11 Anion calibration solutions.

6.11.1 Chlorate, chloride calibration solutions.

Depending on the anion concentration expected, use the stock solutions (6.9) or the mixed standard solution (6.10.1) to prepare 5 to 10 calibration solutions distributed over the expected working range as evenly as possible.

For example, proceed as follow for the range 0,1 mg/l to 1,0 mg/l of ClO_3^- , Cl^- .

Into a series of volumetric flasks of nominal capacity 100 ml, pipette a volume of 1 ml, 2 ml, 3 ml, 4 ml, 5 ml, 6 ml, 7 ml, 8 ml, 9 ml, and 10 ml of the mixed standard solution (6.10.1), add 0,1 ml of sodium hydroxide solution (6.4) and dilute to volume with water (6.1). The concentrations of ClO_3^- and Cl^- in these calibration solutions are 0,1 mg/l, 0,2 mg/l, 0,3 mg/l, 0,4 mg/l, 0,5 mg/l, 0,6 mg/l, 0,7 mg/l, 0,8 mg/l, 0,9 mg/l and 1,0 mg/l respectively.

Prepare the calibration solutions on the day of use.

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6.11.2 Chlorite calibration solutions.

Depending on the anion concentration expected, use the stock solution (6.9) or the chlorite standard solution (6.10.2) to prepare 5 to 10 calibration solutions distributed over the expected working range as evenly as possible.

For example, proceed as follows for the range 0,1 mg/l to 1,0 mg/l ClO_2^- .

Into a series of volumetric flasks of nominal capacity 100 ml, pipette a volume of 1 ml, 2 ml, ml, 3 ml, 4 ml, 5 ml, 6 ml, 7 ml, 8 ml, 9 ml, and 10 ml of the chlorite standard solution (6.10.2), add 0,1 ml of sodium hydroxide solution (6.4) and dilute to volume with water (6.1). The concentrations of ClO_2^- in these calibration solutions are 0,1 mg/l, 0,2 mg/l, 0,3 mg/l, 0,4 mg/l, 0,5 mg/l, 0,6 mg/l, 0,7 mg/l, 0,8 mg/l, 0,9 mg/l and 1,0 mg/l respectively.

Prepare the calibration solutions on the day of use.

6.12 Blank solutions.

Fill a volumetric flask of nominal capacity 100 ml up to volume with water (6.1) and add 0,1 ml of sodium hydroxide solution (6.4).

7 Apparatus

Usual laboratory apparatus, and, the following in particular an ion chromatographic system, complying with the quality requirements of Clause 8. In general, it shall consist of the following components (see Figure 1):

- a) eluent reservoir;

- b) pump, suitable for HPLC;
- c) sample injection system incorporating a sample loop (e.g. sample loop of volume 50 µl);
- d) precolumn (see 10.2), for example, containing the same resin material as the analytical separator column or those being packed with a macroporous polymer;
- e) separator column with the specified separating performance (Clause 8);
- f) conductivity detector (with or without a suppressor device assembly) or UV detector (e.g. spectral photometer; 190 nm to 400 nm) or amperometric detector;
- g) recording device (e.g. recorder, integrator with printer);
- h) cartridges or columns with non-polar phases to be used for sample preparation (e.g. polyvinylpyrrolidone or RP C18¹⁾ cartridges; see 9.1); the use of RP C18 material is restricted by the pH of the eluent; thus, only RP C18 cartridges should be used, and not columns;
- i) cation exchanger in the Ag form (cartridges, 9.2);
- j) cation exchanger in the H form (cartridge, 9.2).

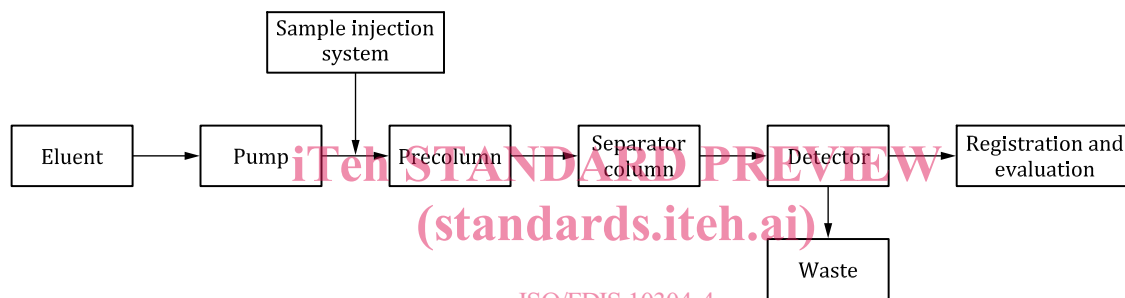


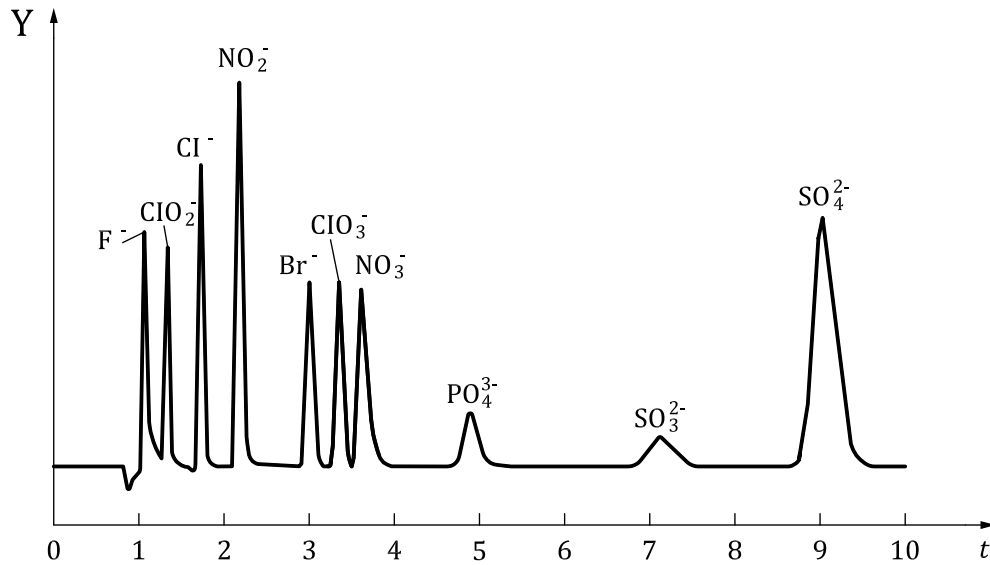
Figure 1 — Schematic representation of an ion chromatography system

8 Quality requirements for the separator column

Separation conditions shall be such that possible interfering anions (fluoride, chlorite, chloride, nitrite, bromide, chlorate and nitrate) at a concentration level of 1 mg/l each (see Figure 2) do not interfere with the anions of interest at a concentration of 1 mg/l.

Regarding chromatograms of samples and standard solutions with higher concentrations, peak resolution R shall not fall below $R = 1,3$ [see Formula (1) and (2) and Figure 3].

1) RP C18 is an example of a suitable product available commercially. This information is given for the convenience of users of this document and does not constitute an endorsement by ISO of this product.



Key

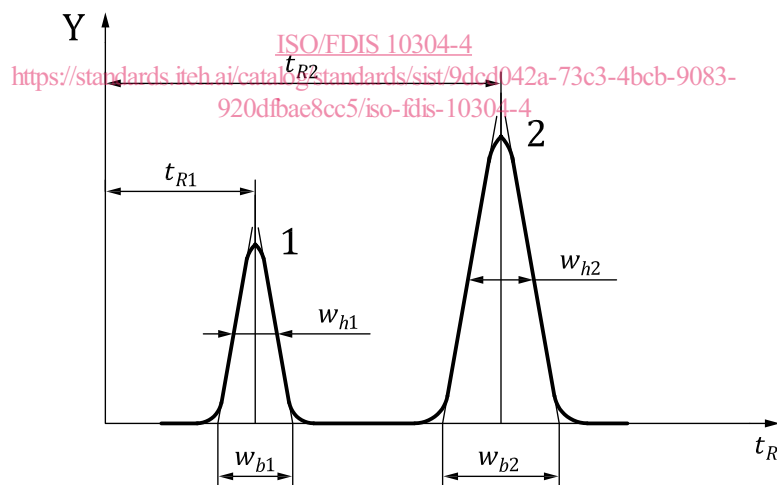
t time, min

Y signal

NOTE Elution sequences and retention times (t_R) can vary, depending on type of column, eluent composition and eluent flow.

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Figure 2 — Example of chromatogram from a column conforming to this document
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Key

Y signal

1 peak 1

2 peak 2

Figure 3 — Graphical representation of parameters used to calculate peak resolution R

Calculate the peak resolution $R_{2,1}$ using [Formula \(1\)](#) or [\(2\)](#).

$$R_{2,1} = 2 \frac{(t_{R2} - t_{R1})}{w_{b2} + w_{b1}} \tag{1}$$