SLOVENSKI STANDARD

oSIST prEN ISO 10304-4:2021

01-februar-2021

Kakovost vode - Določevanje raztopljenih anionov z ionsko tekočinsko kromatografijo - 4. del: Določevanje klorata, klorida in klorita v malo onesnaženih vodah (ISO/DIS 10304-4:2020)

Water quality - Determination of dissolved anions by liquid chromatography of ions - Part 4: Determination of chlorate, chloride and chlorite in water with low contamination (ISO/DIS 10304-4:2020)

Qualité de l'eau - Dosage des anions dissous par chromatographie des ions en phase liquide - Partie 4: Dosage des ions chlorate, chlorure et chlorite dans des eaux faiblement contaminées (ISO/DIS 10304-4:2020)

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ICS:

13.060.50	Preiskava vode na kemične snovi	Examination of water for chemical substances

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DRAFT INTERNATIONAL STANDARD
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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

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

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

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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 of 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 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 10304-4:1997), which has been technically revised.

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

- General: Use of basic text modules and adaption of the structure of the method based on the current layout of ISO/TC 147 standards. None of the amendments do influence e.g. the scope and the quality of the analytical results.
- 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.
- 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.
- 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/elimination 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.

Introduction

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 [4].

DRAFT INTERNATIONAL STANDARD ISO/DIS 10304-4:2020(E)

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).

An appropriate pretreatment 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; λ=207 nm to 220 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. Dilute the sample in to the working range, if necessary.

[b] The minimum working range for chlorite of 0,05 mg/l was obtained using calibration checks, but the round robin trials (Annex A, Table A.4) showed that it is difficult to obtain this with sufficient accuracy. Thus great care shall be taken when working in the lower range of this method.

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*

ISO 10304-1, *Water quality — Determination of dissolved anions by liquid chromatography of ions — Part 1: Determination of bromide, chloride, fluoride, nitrate, nitrite, phosphate and sulfate*

ISO 10304-3, *Water quality — Determination of dissolved anions by liquid chromatography of ions — Part 3: Determination of chromate, iodide, sulfite, thiocyanate and thiosulfate*

ISO 10530, *Water quality — Determination of dissolved sulfide — Photometric method using methylene blue*

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 http://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 life-time 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 chloride / 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 shall have a resistivity of ≥18 MΩ cm (25 °C) and shall not contain particulate matter of a particle size > 0,45 µm.

6.2 Sodium hydrogencarbonate, $NaHCO_3$.

6.3 Sodium carbonate, Na_2CO_3.

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

6.5 Sodium chlorite, $NaClO_2$ (80 %).

6.6 Sodium chloride, NaCl.

6.7 Sodium chlorate, $NaClO_3$.

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.