INTERNATIONAL STANDARD

ISO 10304-4

First edition
1997-12-15

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

Reference number
ISO 10304-4:1997(E)

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.

Draft International Standards adopted by the technical committees are circulated to the member bodies for voting. Publication as an International Standard requires approval by at least 75 % of the member bodies casting a vote.

International Standard ISO 10304-4 was prepared by Technical Committee ISO/TC 147, *Water quality*, Subcommittee SC 2, *Physical, chemical and biochemical methods.*

ISO 10304 consists of the following parts, under the general title *Water quality — Determination of dissolved anions by liquid chromatography of ions:*

— *Part 1: Determination of fluoride, chloride, bromide, nitrate, nitrite, orthophosphate and sulfate in water with low contamination*

— *Part 2: Determination of bromide, chloride, nitrate, nitrite, orthophosphate and sulfate in waste water*

— *Part 3: Determination of chromate, iodide, sulfite, thiocyanate and thiosulfate*

— *Part 4: Determination of chlorate, chloride and chlorite in water with low contamination.*

Annexes A and B of this part of ISO 10304 are for information only.

International Organization for Standardization
Case postale 56 • CH-1211 Genève 20 • Switzerland
Internet central@iso.ch
X.400 c=ch; a=400net; p=iso; o=isocs; s=central

Printed in Switzerland

Introduction

The essential minimum requirements of an ion chromatographic system applied within the scope of this part of ISO 10304 are the following:

- Resolution power of the column:	For the anion to be determined it is essential that the peak resolution does not fall below R = 1,3 (clause 7, figure 3)
- Method of detection:	a) Measurement of the electrical conductivity with or without suppressor device b) Spectrometric measurement (UV/VIS), directly or indirectly c) Amperometric direct detection
- Applicability of the method:	Working ranges according to table 1
- Calibration (9.1):	Calibration and determination of the linear working range (see ISO 8466-1). Use of the method of standard addition to special cases of application (9.2).
- Guaranteeing the analytical quality (9.3):	Validity check of the calibration function. Replicate determinations, if necessary.

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 [2].

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 part of ISO 10304 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*	**Detection**
Chlorate	0,03 to 10	CD
Chloride	0,1 to 50	CD
Chlorite**	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

* The working range is restricted by the ion-exchange capacity of the columns. Dilute the sample in to the working range, if necessary.

** 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 standards contain provisions which, through reference in this text, constitute provisions of this part of ISO 10304. 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 10304 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 5667-2:1991	*Water quality - Sampling - Part 2: Guidance on sampling techniques.*

ISO 5667-3:1994	*Water quality - Sampling - Part 3: Guidance on the preservation and handling of samples.*
ISO 8466-1:1990	*Water quality - Calibration and evaluation of analytical methods and estimation of performance characteristics - Part 1: Statistical evaluation of the linear calibration function.*
ISO 10304-1:1992	*Water quality - Determination of dissolved anions by liquid chromatography of ions - Part 1: Determination of fluoride, chloride, bromide, nitrate, nitrite, orthophosphate and sulfate in water with low contamination*
ISO 10304-2:1995	*Water quality - Determination of dissolved anions by liquid chromatography of ions - Part 2: Determination of bromide, chloride, nitrate, nitrite, orthophosphate and sulfate in waste water*
ISO 10304-3:1997	*Water quality - Determination of dissolved anions by liquid chromatography of ions - Part 3: Determination of chromate, iodide, sulfite, thiocyanate and thiosulfate*
ISO 10530: 1992	*Water quality - Determination of dissolved sulfide - Photometric method using methylene blue.*

3 Interferences

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

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

3.3 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.

3.4 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 (8.2).

3.5 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 8).

Table 2 — Typical cross-sensitivity of anions

Relation of the mass concentration* 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 / 1000 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 / 1000 parts carbonate	CD
1 part chlorite / 1000 parts chloride	CD / UV / AD
1 part chlorite / 100 parts nitrite	AD

* In case the quality requirements in clause 7 (e.g. see figures 2 and 3) are not achieved, the sample shall be diluted.

4 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, 5.11).

Detection is by conductivity (CD), 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).

5 Reagents

Use only reagents of recognized analytical grade. Carry out weighing with an accuracy of 1% of the nominal mass. The water shall have an electrical conductivity of $< 0,01$ mS/m and shall not contain particulate matter of a particle size $> 0,45$ µm. An increase in electrical conductivity due to an uptake of carbon dioxide does not interfere with the determination.

5.1 **Sodium hydrogencarbonate**, $NaHCO_3$

5.2 **Sodium carbonate**, Na_2CO_3

5.3 **Tris(hydroxymethyl)aminomethane**, $NH_2C(CH_2OH)_3$

5.4 **Acetonitrile**, CH_3CN

5.5 **Sodium hydroxide solution**, $c(NaOH) = 0,1$ mol/l

5.6 **Benzoic acid**, $C_7H_6O_2$

5.7 **Potassium hydroxide solution**, $c(KOH)$, = 0,5 mol/l

5.8 **Sodium chlorite**, $NaClO_2$ (80 %)

5.9 **Sodium chloride**, NaCl

5.10 **Sodium chlorate**, $NaClO_3$

5.11 Eluents

Different eluents are used, their choice depending on the type of separator column and detector. Therefore, follow the column manufacturer´s instructions for the exact composition of the eluent. The eluent compositions described in 5.11.1.2, 5.11.1.4, 5.11.2.2 and 5.11.2.3 are examples only.

A selection of reagents for common eluents is presented in 5.1 to 5.7. Preparing eluents from concentrates has proved successful.

Degas all eluents. Take steps to avoid any renewed air pick-up during operation (e.g. by helium sparging). In order to minimize the growth of bacteria or algae, store the eluents in the dark and renew every 3 d.

5.11.1 Examples of eluents for ion chromatography using the suppressor technique

For the application of the suppressor technique, sodium hydroxide and salt solutions of weakly dissociated acids such as sodium carbonate/sodium hydrogencarbonate, sodium hydrogencarbonate, and sodium tetraborate can be used.

5.11.1.1 Sodium carbonate/sodium hydrogencarbonate concentrate

For the eluent concentrate preparation:

Place 19,1 g of sodium carbonate (5.2) and 14,3 g of sodium hydrogencarbonate (5.1) into a graduated flask of nominal capacity 1000 ml, dissolve in water (clause 5) and dilute to volume with water.

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.

5.11.1.2 Sodium carbonate/sodium hydrogencarbonate eluent

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

Pipette 50 ml of the concentrate (5.11.1.1) into a graduated flask of nominal capacity 5000 ml and dilute to volume with water (clause 5).

The solution contains 0,0018 mol/l of sodium carbonate and 0,0017 mol/l of sodium hydrogencarbonate. Store the solution in amber-coloured glass and renew it every 3 d.

5.11.1.3 Sodium hydrogencarbonate concentrate

For the eluent concentrate preparation:

Place 8,4 g of sodium hydrogencarbonate (5.1) into a graduated flask of nominal capacity 1000 ml, dissolve in water (clause 5) and dilute to volume with water.

The solution contains 0,1 mol/l of sodium hydrogencarbonate. This solution is stable for several months if stored at 2 °C to 6 °C.

5.11.1.4 Sodium hydrogencarbonate eluent

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

Pipette 50 ml of the concentrate (5.11.1.3) into a graduated flask of nominal capacity 5000 ml and dilute to volume with water (clause 5).

The solution contains 0,001 mol/l of sodium hydrogencarbonate. Renew the solution every 3 d.

5.11.2 Examples of eluents for ion chromatography without using the suppressor technique

For ion chromatographic systems without suppressor devices, salt solutions, e.g. potassium hydrogenphthalate, *p*-hydroxybenzoic acid, sodium borate/sodium gluconate, potassium hydroxide and sodium benzoate are used. The solutions can contain various additions, e.g. alcohols. The concentration of the salts is usually in the range of 0,0005 mol/l to 0,01 mol/l.

5.11.2.1 Benzoic acid concentrate

For the eluent concentrate preparation:

Place 3,664 g of benzoic acid (5.6) into a beaker of capacity 1000 ml, add approximately 950 ml of water (clause 5). Adjust the pH of the solution to approximately 4,2 with tris(hydroxymethyl)aminomethane (5.3; by adding it either as a solid compound or as a concentrate solution). Stir and dissolve with gentle heating (60 °C to 80 °C). After dissolving, transfer the cool solution into a graduated flask of nominal capacity 1000 ml and add 10 ml of acetonitrile (5.4). Adjust the pH of the solution to 4,6 with tris(hydroxymethyl)aminomethane (5.3; by adding it either as a solid compound or as a solution) and dilute to volume with water (clause 5).

The solution contains 0,03 mol/l of benzoic acid and approximately 1 % of acetonitrile and is stable for one month if stored at 2 °C to 6 °C.

5.11.2.2 Benzoic acid eluent

For the determination of chlorate, chloride and chlorite, the following eluent has proved to be successful:

Place 100 ml of the concentrate (5.11.2.1) and 20 ml of acetonitrile (5.4) into a graduated flask of nominal capacity 1000 ml and dilute to volume with water (clause 5).

The solution contains 0,003 mol/l of benzoic acid and approximately 2 % of acetonitrile. The eluent pH is 4,65. Renew the solution every 7 d.

5.11.2.3 Potassium hydroxide eluent

For the determination of chlorate, chloride and chlorite, the following eluent has proved to be successful:

Place 500 ml of water (clause 5) into a graduated flask of nominal capacity 1000 ml, add 10 ml of the potassium hydroxide solution (5.7) and dilute to volume with water.

The solution contains 0,005 mol/l of potassium hydroxide. Renew the solution every 3 d.

5.12 Stock solutions

Prepare stock solutions of concentration ρ = 1000 mg/l for each of the anions chlorate, chloride and chlorite.

Dissolve the appropriate mass of each of the substances (5.8, 5.9, 5.10), prepared as stated in table 3, in approximately 800 ml of water (clause 5, degassed with nitrogen or helium), in graduated flasks of nominal capacity 1000 ml, add 1 ml of sodium hydroxide solution (5.5). Dilute to volume with water. The solutions are stable as indicated in table 3.

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

Table 3 — Mass of portion, pretreatment and storage suggestions for stock solutions

Anion	**Compound**	**Concentration derived from subst.-portion** g/l	**Pretreatment**	**Storage**
Chlorate	$NaClO_3$	1,2753 ± 0,013	Dry in a desiccator only!	In glass for 1 month if kept at 2 °C to 6 °C
Chloride	NaCl	1,6484 ± 0,017	Dry at 105 °C	In polyethylene for 3 months if kept at 2 °C to 6 °C
Chlorite*	$NaClO_2$	approx. 1,7	Dry in a desiccator only!	In glass for 1 week if kept at 2 °C to 6 °C in the dark

*The concentration of the chlorite stock solution shall be determined iodometrically before use (see ISO 10530, annex A).

5.13 Standard solutions

Depending upon the concentrations expected, prepare standard solutions of different anion composition and concentration from the stock solutions (5.12). The risk of changes in concentration caused by interaction with the vessel material increases with decreasing anion concentration. Store the standard solutions in polyethylene (PE) vessels. Take into account that sodium chlorite salt can contain up to 20 % sodium chloride. Prepare chlorite standard solutions as described in 5.13.2 to avoid chloride contamination, e.g. of the mixed standard solution (5.13.1).

5.13.1 Mixed standard solution of chlorate and chloride

The mass concentrations of this solution are as follows:

$$\rho(ClO_3^-, Cl^-) = 10 \text{ mg/l}$$

Pipette 1 ml of each of the chlorate and chloride stock solutions (5.12) into a graduated flask of nominal capacity 100 ml, add 0,1 ml of sodium hydroxide solution (5.5) and fill up to volume with water (clause 5).

Prepare the solution on the day of use.

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

5.13.2 Chlorite standard solution

The mass concentration of this solution is as follows:

$$\rho(\mathrm{ClO_2^-}) = 10 \text{ mg/l}$$

Pipette 1 ml of chlorite stock solution (5.12) into a graduated flask of nominal capacity 100 ml, add 0,1 ml of sodium hydroxide solution (5.5) and make up to volume with water (clause 5).

Prepare the solution on the day of use.

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

5.14 Anion calibration solutions

5.14.1 Chlorate, chloride calibration solutions

Depending on the anion concentration expected, use the stock solutions (5.12) or the mixed standard solution (5.13.1) 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 $\mathrm{ClO_3^-}$, $\mathrm{Cl^-}$.

Into a series of graduated 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 (5.13.1), add 0,1 ml of sodium hydroxide solution (5.5) and dilute to volume with water (clause 5). The concentrations of $\mathrm{ClO_3^-}$ and $\mathrm{Cl^-}$ 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.

5.14.2 Chlorite calibration solutions

Depending on the anion concentration expected, use the stock solution (5.12) or the chlorite standard solution (5.13.2) 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 $\mathrm{ClO_2^-}$:

Into a series of graduated flasks of nominal capacity 100 ml, pipette a volume of 1 ml, 2 ml, ml, 4 ml, 5 ml, 6 ml, 7 ml, 8 ml, 9 ml, and 10 ml of the chlorite standard solution (5.13.2), add 0,1 ml of sodium hydroxide solution (5.5) and dilute to volume with water (clause 5). The concentrations of $\mathrm{ClO_2^-}$ 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.

5.15 Blank solutions

Fill a graduated flask of nominal capacity 100 ml up to volume with water (clause 5) and add 0,1 ml of sodium hydroxide solution (5.5).

6 Apparatus

Usual laboratory apparatus, and, in particular

6.1 Ion chromatographic system, complying with the quality requirements of clause 7. In general, it shall consist of the following components (see figure 1):

a) Eluent reservoir;