INTERNATIONAL STANDARD

ISO 10304-4

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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

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.

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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 0,1 to 1 0,01 to 1	CD UV; λ=207 nm to 220 nm 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:

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

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 ClO_3^-, 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 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.

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 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 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;

b) Pump, suitable for HPLC;

c) Sample injection system incorporating a sample loop (e.g. sample loop of volume 50 µl);

d) Precolumn (see 9.2) e.g. containing the same resin material as the analytical seperator column or those being packed with a macroporous polymer;

e) Separator column with the specified separating performance (clause 7);

f) Conductivity detector (with or without a suppressor device assembly) or UV detector (e.g. spectral photometer; 190 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 RPC18[1] cartridges; 8.1.9);

i) Cation exchanger in the Ag form (cartridge; 8.2);

j) Cation exchanger in the H form (cartridge, 8.2).

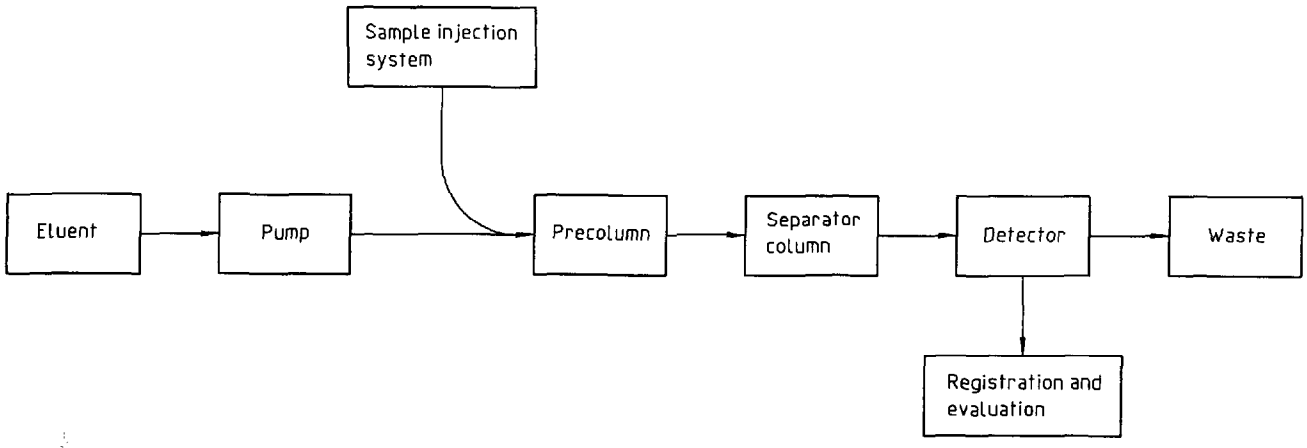


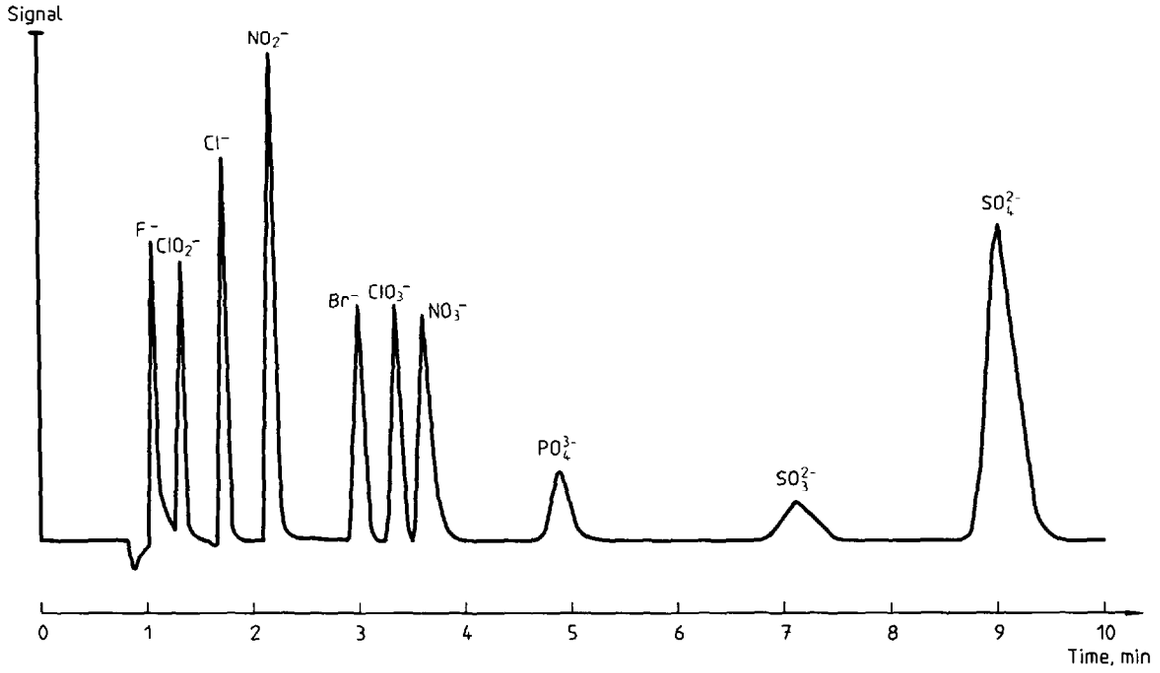
Figure 1 — Schematic representation of an ion chromatography system

7 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 equation (1) and figure 3].

[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.



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

Figure 2 — Example of chromatogram from a column conforming to this part of ISO 10304

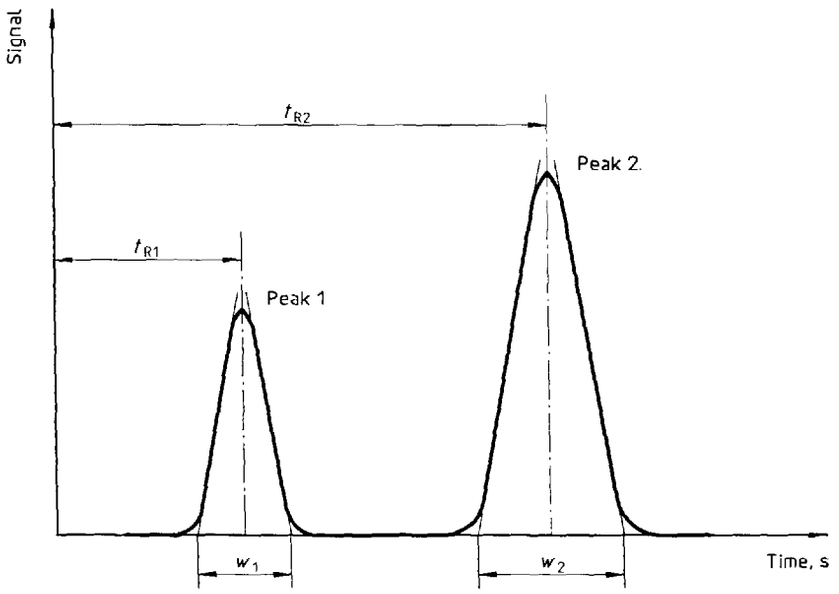


Figure 3 — Graphical representation of parameters used to calculate peak resolution *R*

Calculate the peak resolution R using equation (1).

$$R_{2,1} = \frac{2(t_{R2} - t_{R1})}{(w_2 + w_1)} \quad (1)$$

where

$R_{2,1}$ is the resolution for the peak pair 2,1;

t_{R1} is the retention time, in seconds, of the first peak;

t_{R2} is the retention time, in seconds, of the second peak;

w_1[2] is the peak width, in seconds, on the time axis of the first peak;

w_2[2] is the peak width, in seconds, on the time axis of the second peak.

8 Sampling and sample pretreatment

8.1 General requirements

8.1.1 It is important to ensure that the laboratory receives a sample which is truly representative and has not been damaged or changed during transport or storage. Sampling is not part of the method specified in this part of ISO 10304.

8.1.2 Use clean polyethylene or glass vessels for sampling.

8.1.3 After sample collection, adjust the pH of the samples to a value of 10 ± 0,5 with sodium hydroxide solution (5.5).

NOTE Be aware of Cl^- contamination when using pH-electrodes.

8.1.4 After the arrival of the sample in the laboratory, filter it through a membrane filter (of pore size 0,45 µm) to prevent adsorption of the anions onto particulate matter or conversion of anions by bacterial growth.

8.1.5 If an immediate analysis is not feasible, stabilize the membrane-filtered sample by cooling it (2 °C to 6 °C) or deep-freezing (−16 °C to −20 °C), provided this procedure will not impair the results.

8.1.6 To avoid precipitation during analysis caused by changing pH values, check the sample pH prior to injection,and adjust the pH of the sample to the pH of the eluent if necessary (see 5.11).

8.1.7 Prior to injection into the analyser, filter the sample again through a membrane filter (of pore size 0,45 µm) to remove any particulate matter if present.

8.1.8 Avoid contamination of the sample from the membrane (e.g. rinse the membrane with a small amount of the sample itself, and discard the first portion of the filtrate).

8.1.9 Waters strongly contaminated with organics can damage the separator column. In this case it is advisable to dilute the sample and to filter it via a nonpolar phase [e.g. polyvinylpyrrolidone, 6.1 h)] prior to injection (9.2).

8.1.10 Treat blank (5.15) and calibration solutions (5.14) in the same manner as the sample solutions.

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[2] w_1, w_2 are the widths of the base of the isosceles triangle constructed representing 4 times the standard deviation of the Gaussian peak.

8.1.11 Continue with 8.2 if elevated levels of chloride or bromide interfere with the determination of chlorite or chlorate.

8.2 Sample pretreatment in the case of elevated levels of chloride and bromide

If levels of chloride or bromide are such that peak resolution is no longer acceptable (see clause 7), reduce their levels by the use of a cation exchanger as follows:

a) dilute the sample if necessary, and run it through a strongly acidic cation exchanger in the Ag form[3] [cartridge, 6.1 i)] to remove dissolved halides from the sample;

b) run the filtrate through a cation exchanger in the H form[3] [cartridge, 6.1 j)] to remove dissolved silver ions from the eluate;

c) chromatograph the treated sample as described in clause 9;

d) treat blank solution (5.15) and calibration solution (5.14) in the same manner.

9 Procedure

Set up the ion chromatograph (6.1) according to the instrument manufacturer's instructions (e.g. the instrument is ready for operation as soon as the baseline is stable). Perform the calibration described in 9.1. Measure samples and blank solutions (5.15) as described in 9.2.

9.1 Calibration

Inject the calibration solutions. Identify the peaks for particular anions by comparing the retention times with those of the standard solutions (see 5.14). Take into account the fact that the retention times can be dependent on concentration and matrix. In calculating concentrations, use the characteristic that the area (or height) of the peak (signal) is proportional to the concentration of the anion.

When the analytical system is first evaluated, and at intervals afterwards, establish a calibration function (see ISO 8466-1) for the measurement as follows.

9.1.1 Prepare calibration solutions as described in 5.14.

9.1.2 Analyse the calibration solutions chromatographically.

9.1.3 Use the data obtained to calculate the regression line. Reject if it is not linear (for linearity criteria, refer to ISO 8466-1). Equation (2) (calibration function) applies for the ion i to be determined:

$$Y_i = b_i \rho_i + a_0 \qquad (2)$$

where:

Y_i is the measured value (size of signal), in terms of peak height or peak area, expressed in millimetres or microvolt seconds, respectively;

b_i is the slope of the calibration function, e.g. mm • l/mg; µV • s • l/mg;

ρ_i is the mass concentration, in milligrams per litre, of the ion i;

a_o is the ordinate intercept of the calibration function (calculated blank), expressed e.g. in millimetres or microvolt seconds.

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[3] Before use rinse with water (clause 5).

9.1.4 Subsequently, check the continuing validity of the established calibration function (9.3).

9.2 Measurement of samples using the standard calibration procedure

After establishing the calibration function, inject the pretreated sample (clause 8) into the chromatograph and measure the peaks as above (clause 9).

In general the use of a precolumn is strongly recommended, especially for the injection of waters strongly contaminated with organics (8.1.9), in order to protect the analytical separator column. Two different types of precolumns can be used: those containing the same resin material as the analytical separator column and those packed with a macroporous polymer (6.1).

If the ion concentration of the sample to be analysed exceeds the calibration range, dilute the sample and analyse it. Sometimes it is necessary to establish a separate calibration function for the lower concentration range.

If matrix interferences are expected, use the method of standard addition to safeguard the results (verify the peaks by comparing the retention times of the spiked sample with those of the original sample).

Measure the blank solution (5.15) in the same manner.

9.3 Validity check of the calibration function

In order to verify the continuing validity of the calibration function, measure a minimum of two calibration solutions of different concentrations in the lower and upper parts of the working range. This should take place after the setup procedure (clause 9) and after each sample series (9.2) at least, but in any case after 20 measurements or 5 in case of amperometric detection.

Calculate the mass concentrations of the analysed calibration solutions using the inverse calibration function [see clause 10, equation (3)]. The concentrations shall be in the range of the confidence band. If the calibration function is not valid, carry out a new calibration (9.1).

10 Calculation

Estimate the mass concentration, ρ_i, in milligrams per litre, of the anion in the solution using the peak areas or peak heights and the inverse calibration equation (3) (9.1.3) as follows:

$$\rho_i = \frac{y_i - a_o}{b_i} \qquad (3)$$

For an explanation of the variables see equation (2).

Take into account all of the dilution steps.

11 Expression of results

Report the results to a maximum of two significant figures.

Example:

Chlorate (ClO_3^-) 0,050 mg/l

Chloride (Cl^-) 35 mg/l

Chlorite (ClO_2^-) 0,15 mg/l

12 Test report

The test report shall contain at least the following information:

a) a reference to this part of ISO 10304;

b) identity of the water sample;

c) expression of the results according to clause 11;

d) description of sample pretreatment, if relevant;

e) description of the chromatographic conditions: type of instrument and column, column dimensions, eluent flowrate, type of detector and detector parameters;

f) description of the method used for the evaluation (peak height or peak area);

g) calculation of the results (linear calibration function, method of standard addition);

h) any deviation from this method and information on all circumstances which may have influenced the results.

Annex A
(informative)

Interlaboratory trial

An interlaboratory trial was organized in Germany in 1996 with laboratories from France and Germany participating. A variety of instruments and other analytical conditions were used which conformed with the quality parameters specified in the method given in this part of ISO 10304.

For the description of sample matrix see table A.1.

The statistical data of results are presented in tables A.2 to A.4.

The coefficients of variation of the procedure V_{xo} (obtained from determined calibration functions analogous to those described in 9.1) are listed in table A.5. The data came from laboratories participating in the interlaboratory trial in Germany in 1996.

Table A.1 — Description of sample matrix

Parameter	Sample No.			
	1 and 2	3 and 4	5 and 6	7 and 8
	Sample matrix			
	Synthetic water	Drinking water	River water	Swimming pool water
Base-capacity (mmol/)	0,09	0,39	1,24	0,12
Acid-capacity (mmol/l)	0,22	2,75	3,79	0,29
$\Sigma(Ca^{2+}+Mg^{2+})$ (mmol/l)	0,61	7,7	10,6	0,82
Hydrogencarbonate (mg/l)	13,3	167,3	231,2	17,8
Fluoride (mg/l)	0,12	0,25	0,13	0,05
Chloride (mg/l)	16,1	59,5	68,4	80,2
Nitrate (mg/l)	18,5	4,8	21,8	11,6
Phosphate (mg/l)	0,27	0,05	0,48	0,12
Sulfate (mg/l)	35,1	81,7	58,9	15,7
Bromide (mg/l)	0,21	0,06	0,08	0,005
Chlorate (mg/l)	----	----	----	0,08
Chlorite (mg/l)	----	----	----	----
Sodium (mg/l)	21,5	82,5	82,1	15,1
Potassium (mg/l)	31,7	3,6	4,5	2,5
Magnesium (mg/l)	-----	23,0	14,8	12,1
Calcium (mg/l)	-----	14,1	52,1	26,3
DOC (mg/l)	0,27	0,52	0,95	0,7

Table A.2 — Statistical data for chlorate

Sample	Matrix	*N*	*L*	KA_1 %	x_{ref} mg/l	$\bar{x}$ mg/l	WFR %	s_R mg/l	CV_R %	s_r mg/l	CV_r %
1	Synthetic water	84	21	0,0	0,080	0,0752	94,0	0,0171	22,77	0,0060	8,01
2	Synthetic water	80	20	0,0	0,200	0,1830	91,5	0,0381	20,84	0,0156	8,50
3	Drinking water	79	20	9,2	0,091	0,0902	99,1	0,0165	18,31	0,0091	10,08
4	Drinking water	87	22	1,1	0,210	0,2001	95,7	0,0455	22,63	0,0200	9,97
5	River water	79	20	6,0	0,080	0,0754	94,2	0,0172	22,87	0,0067	8,94
6	River water	84	21	0,0	0,200	0,1827	91,4	0,0440	24,08	0,0131	7,17
7	Swimming pool water	88	22	0,0	0,159	0,1438	90,4	0,0266	18,50	0,0140	9,74
8	Swimming pool water	87	22	0,0	0,280	0,2672	95,4	0,0468	17,51	0,0203	7,60

N is the number of analytical values per level

L is the number of participating laboratories

KA_1 is the percentage of outlying values from the replicate determinations

x_{ref} is the nominal value of the analytical sample, determined by reference procedure

$\bar{x}$ is the total mean

WFR is the recovery rate (%)

s_R is the standard deviation of the reproducibility

CV_R is the coefficient of variation of the reproducibility

s_r is the standard deviation of the repeatability

CV_r is the coefficient of variation of the repeatability

NOTE All samples spiked with ClO_3^-, ClO_2^-, NO_3^-, Br^- mixed standard solution.

Table A.3 — Statistical data for chloride

Sample	Matrix	N	L	KA_1 %	x_{ref} mg/l	x mg/l	WFR %	s_R mg/l	CV_R %	s_r mg/l	CV_r %
1	Synthetic water	104	26	0,0	16,100	16,2308	100,8	0,8369	5,16	0,2989	1,84
2	Synthetic water	104	26	0,0	16,100	16,3244	101,4	0,8763	5,37	0,3320	2,03
3	Drinking water	96	24	7,7	59,500	59,6099	100,2	1,9158	3,21	0,7913	1,33
4	Drinking water	91	23	12,5	59,500	59,5080	100,0	1,5999	2,69	0,5776	0,97
5	River water	95	24	8,7	68,400	68,4916	100,1	1,9975	2,92	0,8017	1,17
6	River water	100	25	3,8	68,400	68,2539	99,8	2,0774	3,04	0,9878	1,45
7	Swimming pool water	104	26	0,0	80,200	79,6175	99,3	3,3315	4,18	1,6512	2,07
8	Swimming pool water	91	23	12,5	80,200	79,5848	99,2	1,9850	2,49	1,0022	1,26

NOTE 1 Definition of symbols see table A.2.

NOTE 2 All samples spiked with ClO_3^-, ClO_2^-, NO_3^-, Br^- mixed standard solution.

Table A.4 — Statistical data for chlorite

Sample	Matrix	N	L	KA_1 (%)	x_{ref} mg/l	x mg/l	WFR %	s_R mg/l	CV_R %	s_r mg/l	CV_r %
1	Synthetic water	92	23	8,0	0,100	0,1054	105,4	0,0214	20,27	0,0059	5,64
2	Synthetic water	88	22	12,0	0,300	0,3079	102,6	0,0266	8,64	0,0082	2,66
3	Drinking water	80	20	13,0	0,100	0,1248	124,8	0,0506	40,51	0,0088	7,05
4	Drinking water	76	19	17,4	0,300	0,3214	107,1	0,0467	14,54	0,0103	3,20
5	River water	80	20	13,0	0,100	0,1116	111,6	0,0368	32,99	0,0059	5,27
6	River water	75	19	18,5	0,300	0,3113	103,8	0,0375	12,06	0,0123	3,96
7	Swimming pool water	91	23	8,1	0,100	0,1012	101,2	0,0291	28,74	0,0058	5,75
8	Swimming pool water	86	22	13,1	0,300	0,3004	100,1	0,0293	9,75	0,0081	2,71

NOTE 1 Definition of symbols see table A.2.

NOTE 2 All samples spiked with ClO_3^-, ClO_2^-, NO_3^-, Br^- mixed standard solution.

Table A.5 — Estimation of performance characteristics indicated by coefficients of variation of the procedure (V_{xo})

Anion	Range of V_{xo} %	Examined working ranges mg/l
Chlorate (ClO_3^-)	0,57 to 3,9	0,03 to 0,30
	1,1 to 3,2	0,1 to 1,0
Chloride (Cl^-)	0,21 to 3,6	10 to 100
Chlorite (ClO_2^-)	0,61 to 4,2	0,05 to 0,50

Annex B
(informative)

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