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Water quality — Determination of dissolved perchlorate — Method using ion chromatography (IC)

Qualité de l'eau — Détermination du perchlorate dissous — Méthode par chromatographie ionique (IC)

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Foreword

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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*.

Water quality — Determination of dissolved perchlorate — Method using ion chromatography (IC)

WARNING — Persons using this document should be familiar with normal laboratory practice. This document does not purport to address all of the safety problems, if any, associated with its use. It is the responsibility of the user to establish appropriate safety and health practices and to determine the applicability of any other restrictions.

IMPORTANT — It is absolutely essential that tests conducted in accordance with this document be carried out by suitably qualified staff.

1 Scope

This document specifies a method for the determination of dissolved perchlorate in water (e.g. drinking water, mineral water, raw water, surface water, partially treated water or swimming pool water, waste water from drinking/swimming pool water treatment plants).

Appropriate pre-treatment of the sample (e.g. matrix elimination) allows a direct determination of perchlorate ≥ 1 µg/l.

The working range is restricted by the ion-exchange capacity of the separator column. Dilution of the sample to the working range can be necessary.

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 3696, *Water for analytical laboratory use — Specification and test methods*

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 8466-2, *Water quality — Calibration and evaluation of analytical methods and estimation of performance characteristics — Part 2: Calibration strategy for non-linear second-order calibration functions*

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:

— IEC Electropedia: available at http://www.electropedia.org/

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

4 Interferences

Perchlorate is known to be susceptible to microbiological degradation in the absence of nitrate and by anaerobic bacteria (References [5] and [6]).

Any substance that has a retention time coinciding with perchlorate and producing a detector response can interfere. Co-elution can be solved by changing separator columns, eluent strength (e.g. gradient elution), modifying the eluent with organic solvents or by selective removal of the interference by sample pre-treatment.

Higher chloride, sulfate, nitrate, orthophosphate, hydrogen carbonate and carbonate concentrations (e.g. 1 g/l) can interfere with the determination of perchlorate (co-elution) or can have an impact on the retention time or the peak shape (distortion) or recovery of perchlorate. This effect can be checked for every matrix by standard addition and the recovery of perchlorate should be within 85 % to 115 %. Interferences can be reduced by sample dilution or with the aid of special cation exchangers (see 7.2 and Clause 9) or be resolved by the application of advanced inline cutting or re-injection techniques (see Annexes A, B and C).

Metals like iron or aluminium present in samples and eluent will bind to the resin material of the separator column or suppressor resulting in a loss of performance. Metal ions can be eliminated with the aid of special cation exchangers (see Annex A and Clause 9).

Solid particles and organic compounds (such as mineral oils, detergents and humic acids) shorten the lifetime of the pre-column and the separator column (see Clause 9).

5 Principle

The method requires the application of high-capacity separator columns which allow the injection of sample volumes, e.g. up to 4 ml.

If necessary, the sample is pre-treated in order to remove anions, metals, organics and solids (see Clause 9).

Measurement of perchlorate is performed with or without matrix elimination and with or without pre-concentration (see 10.3 and Annexes A, B and C).

Perchlorate is separated by ion chromatography (IC) with suppressed conductivity detection (CD).

As stationary phase, an anion exchange resin is used. Aqueous solutions of salts of monobasic acids and dibasic acids are used as eluents for isocratic or gradient elution e.g. carbonate-, hydrogen carbonate-, hydroxide-eluent and an organic modifier like acetone or acetonitrile (6.3).

Resolution, *R*, shall be checked to ensure that it complies with the required separation conditions (8.1).

The concentration of perchlorate is determined after a calibration according to ISO 8466-1 or ISO 8466-2.

Control experiments are necessary to check the validity of the calibration function. Replicate determinations can be necessary. The method of standard addition can be applied if matrix interferences are expected.

6 Reagents

Use only reagents of pro analysis grade free of compounds containing perchlorate. Weigh the reagents with an accuracy of ±1 % of the nominal mass, unless stated otherwise. Prepare alternative concentrations or volumes of solutions as described in 6.3 to 6.5, if necessary. Alternatively, use commercially available solutions of the required concentration.

6.1 Water, ISO 3696, grade 1 and with a resistivity of ≥ 18,2 MΩ cm (25 °C).

6.2 Sodium perchlorate, $NaClO_4$, > 99 %.

6.3 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 an organic modifier, 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 8.1. Use eluents as long as the requirements in Clause 8 and in 10.3 are met.

An example for an appropriate eluent manually prepared is given in 6.3.2.

6.3.1 **Sodium hydroxide solution**, w(NaOH) = 50 %.

6.3.2 **Sodium hydroxide eluent**, ρ(NaOH) = 0,05 mol/l.

Dissolve 4 g of sodium hydroxide solution (6.3.1) in approximately 900 ml of water (6.1) in a 1 000 ml volumetric flask and dilute to volume with water (6.1). Mix and degas, e.g. by sparging with helium for approximately 10 min. Store the eluent in a glass or polyethene eluent reservoir under an inert helium atmosphere to minimize carbonate contamination. Prepare the eluent on the day of use.

NOTE Solutions of manually prepared sodium hydroxide can be susceptible to carbonate contamination resulting from adsorption of carbon dioxide from the atmosphere. This contamination can lead to irreproducible perchlorate retention times, elevated instrument background conductivity and increased baseline noise/drift.

6.4 Perchlorate standard solution.

Depending on the concentrations expected, prepare the following standard solutions of different perchlorate concentrations from the stock solution (6.4.1). Note the possible risk of changes in concentration caused by interaction with the vessel material which will increase with decreasing perchlorate concentration. Store the standard solutions in polyethene or glass bottles.

6.4.1 **Perchlorate stock solution**, $\rho\left(ClO_4^-\right)$ = 1 000 mg/l.

Dry approximately 1,5 g sodium perchlorate (6.2) at (110 ± 5) °C for 2 h. Dissolve (1,231 ± 0,001) g of the dried sodium perchlorate in approximately 800 ml of water (6.1) in a 1 000 ml volumetric flask and dilute to volume with water (6.1).

Store the solution at 2 °C to 8 °C in polyethene or glass bottles. The solution is stable for 12 months.

6.4.2 **Perchlorate standard solution I**, $\rho\left(ClO_4^-\right)$ = 100 mg/l.

Pipette 10,0 ml of sodium perchlorate stock solution (6.4.1) into a 100 ml volumetric flask and dilute to volume with water (6.1).

Store the solution at 2 °C to 8 °C in polyethene or glass bottles. The solution is stable for six months.

6.4.3 **Perchlorate standard solution II**, $\rho\left(ClO_4^-\right)$ = 1 mg/l.

Pipette 1,0 ml of standard solution I (6.4.2) into a 100 ml volumetric flask, dilute to volume with water (6.1).

Store the solution at 2 °C to 8 °C in polyethene or glass bottles. The solution is stable for three months.

6.5 Perchlorate calibration solutions

Depending on the perchlorate concentration expected in the sample, use the perchlorate standard solutions I or II (6.4.2 or 6.4.3) 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 1 µg/l to 5,5 µg/l perchlorate. Pipette into a series of 100 ml volumetric flasks the volumes described in Table 1.

Table 1 — Example for the preparation of calibration solutions

Volume standard solution II (6.4.3)	100 µl	150 µl	200 µl	250 µl	300 µl	350 µl	400 µl	450 µl	500 µl	550 µl
$\rho\left(ClO_4^-\right)$ (µg/l)	1	1,5	2	2,5	3	3,5	4	4,5	5	5,5

Prepare the calibration solutions on the day of use.

6.6 Blank solution

Fill a volumetric flask (e.g. 100 ml) with water (6.1).

7 Apparatus

The usual laboratory apparatus and, in particular, the following.

7.1 Ion chromatographic system, complying with the quality requirements given in Clause 8, i.e. resolution. In general, it shall consist of the following components (see Figure 1).

7.1.1 Separator column, with the specified separating performance (8.1).

7.1.2 Precolumn, if necessary (see Clause 4).

NOTE The use of a precolumn is advantageous not only for the analyses of waters highly loaded with organics (see Clause 4). It serves as well to protect the separator column. In general, two different types of precolumns are available: those containing the same or similar resin material as the separator column, and those packed with a non-functionalised resin.

7.1.3 Conductivity detector (CD), with a suppressor device.

7.1.4 Eluent reservoir and a degassing unit.

7.1.5 IC-pump, suitable for isocratic or gradient technique, respectively.

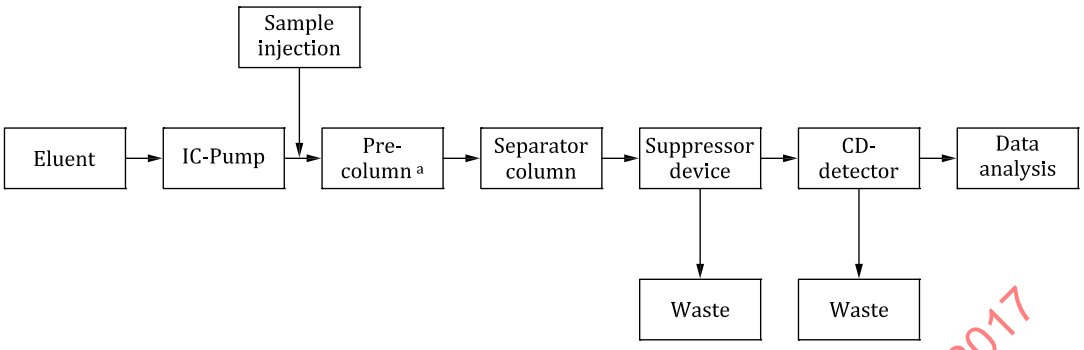
7.1.6 Sample delivery device, e.g. sample pump, including a sample injection system incorporating a sample loop of appropriate volume (e.g. 1 ml to 4 ml) or an autosampler device.

7.1.7 Recording device, e.g. PC with software for chromatography data acquisition and evaluation.

7.2 SPE-cartridges.

7.2.1 Cation exchanger in the Na-form, optional: metal clean up column for inline use.

7.2.2 Cartridges, with non-polar phases to be used for sample preparation (e.g. polyvinylpyrrolidone, RP C18).



a Optional.

Figure 1 — Schematic representation of an ion chromatographic system

8 Quality requirements

8.1 Performance of the separator column

In chromatograms of samples and standard solutions, the peak resolution, R, between the anion of interest and its nearest peak shall not fall below 1,3 (see Formula (1) and Figure 2). Separation conditions shall be such that possible interfering anions will not interfere with the anion of interest.

If R fails the criteria ≥ 1,3 or perchlorate elutes as a rider peak (see Figure A.1) due to higher concentrations of matrix ions (e.g. chloride, sulfate, nitrate and carbonate), then if necessary,

— dilute the sample,

— change separator columns,

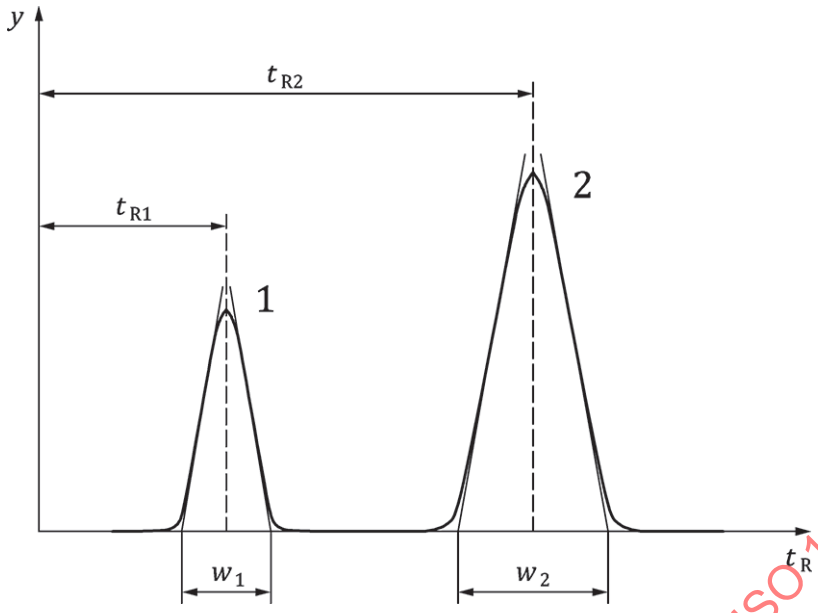
— change the eluent strength (e.g. gradient elution),

— modify the eluent with organic solvents,

— remove the interference selectively by sample pre-treatment (Annex A), and/or

— apply column cut or re-injection techniques according to Annex B or Annex C, and

— determine recovery or apply standard addition.



Key

w_1 width of peak 1
w_2 width of peak 2
t_R retention time, in seconds
y signal
1 peak 1
2 peak 2

Figure 2 — Graphical representation of the parameters to calculate the peak resolution, *R*

NOTE 1 Within the scope of this document, the calculation of resolution, R, is appropriate for both isocratic and gradient elution.

Calculate the peak resolution $R_{2,1}$ for the peak pair 2,1 using Formula (1):

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

where

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 is the peak width, in seconds, on the time axis of the first peak;

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

NOTE 2 w_1, w_2 being the base width of the constructed isosceles triangle over each Gaussian peak.

8.2 Materials

All materials used shall not add a positive or negative bias to the perchlorate result.

9 Sampling and sample pre-treatment

Use clean vessels (e.g. glass, polyethene, polypropene, PTFE) for sampling.

Perchlorate is known to be susceptible to microbiological degradation in absence of nitrate and by anaerobic bacteria (see References [5] and [6]). If necessary, reduce these risks by filtering the sample using a 0,2 µm membrane filter at the sampling site. Store the sample with headspace to reduce the potential for degradation by any remaining organisms (see References [5] and [6]). Cooling the sample during transportation is advisable.

If necessary, eliminate metals with the aid of cation exchangers (e.g. SPE-cartridge in the Na-form).

If necessary, remove solids with the aid of a membrane filter of pore size 0,45 µm.

NOTE Hydrophilic polypropylene or polyethersulfonate filters can be applied as they have been proved acceptable. The use of a polyvinylidene fluoride (PVDF) filter can cause total loss of perchlorate (see Reference [7]). If necessary, remove organic compounds and solids with the aid of a non-polar adsorbent (e.g. SPE-cartridge, column) or dialysis.

Analyse the sample within 28 d after sampling.

10 Procedure

10.1 General

Set up the ion chromatographic system (7.1) in accordance with the instrument manufacturer's instructions.

Run the eluent. Once the baseline is stable, analysis can begin.

Perform the calibration as given in 10.2. Measure the samples and blank solution (6.6) according to 10.3.

10.2 Calibration

Inject the perchlorate calibration solutions (6.5). The measured signal (peak area or peak height) is proportional to the perchlorate concentration.

When the analytical system is first started up and at intervals afterwards, establish a calibration function (see ISO 8466-1 or ISO 8466-2).

Use the data obtained (peak area or peak height) to calculate the regression line as specified in ISO 8466-1 or ISO 8466-2.

Subsequently, verify the continuing validity of the established calibration function (10.4).

NOTE Generally, the calibration method is not restricted to a calibration strategy covering a single concentration decade as specified in ISO 8466-1 or ISO 8466-2 only. When calibrating over a larger range than one concentration decade, a loss of accuracy, compared to that specified in ISO 8466-1 or ISO 8466-2, can occur.

10.3 Measurement of perchlorate

After establishing the calibration function, inject the sample into the chromatograph and measure the peaks as described above. Prior to injection into the analyser, filter the sample through a membrane filter (pore size according to the manufacturer's instruction) to remove any particulate matter, if necessary. Prevent possible contamination of the sample from the membrane (e.g. rinse the membrane with a small volume of the sample and discard the first portion of the filtrate).

Identify the perchlorate peak by comparing the retention time with that of perchlorate in the calibration solutions (6.5). Deviation of retention times shall not exceed ±10 % within a batch.

If the perchlorate concentration of the sample exceeds the calibration range, dilute the sample and re-analyse.

If the sperchlorate concentration of the sample falls lower than the calibration range, establish a separate calibration function for the lower working range, if necessary.

Matrix interferences can be solved according to Clause 8.

If an influence of matrix components on the perchlorates retention time is suspected, apply the method of standard addition to confirm the results (verify the peaks by comparing the retention time of the spiked sample with those of the original sample).

Measure the blank solution (6.6) in the same way.

10.4 Validity check of the calibration function

In order to verify the validity of the calibration function, measure independent standard solutions of different perchlorate concentrations in the lower and upper third of the working range. Proceed accordingly after the set up procedure (10.1) and after each sample series at least, but in any case, after 20 measurements. Recovery shall be within 85 % to 115 % of the nominal value. Recalibrate, if necessary. Replicate determinations can be necessary.

11 Calculation

Calculate the mass concentration, ρ, in micrograms or milligrams per litre of perchlorate in the solution using the peak areas or peak heights and calibration function as specified in ISO 8466-1 or ISO 8466-2 (10.2).

Take into account all of the dilution steps.

12 Expression of results

Results shall be reported to a maximum of two significant figures.

EXAMPLE

Perchlorate $\left(ClO_4^-\right)$ 15 µg/l

Perchlorate $\left(ClO_4^-\right)$ 1,8 µg/l

13 Test report

The test report shall contain at least the following information:

a) the test method used, together with a reference to this document, i.e. ISO 19340;

b) identity of the sample;

c) expression of the results according to Clause 12;

d) description of sample pre-treatment, if relevant;

e) any deviation from this method;

f) report of all circumstances that can have affected the results.

Annex A
(normative)

Elimination of dissolved sulfate, chloride, hydrogen carbonate, carbonate and metals

A.1 General

This annex specifies the determination of perchlorate using offline matrix elimination.

The requirements given in Clauses 1 to 13 remain valid.

A.2 Scope

See Clause 1 and the following.

This modification is applicable for samples with higher loads of dissolved salts (e.g. chloride, sulfate, carbonate) causing interference with the perchlorate determination applying sample injection volumes up to 4 ml. The method is applicable for the determination of perchlorate concentrations ≥ 1 µg/l.

A.3 Principle

See Clause 5 and the following.

Decrease the dissolved salt concentrations using cation exchange SPE-cartridges.

A.4 Reagents

See Clause 6 and the following.

A.4.1 Calcium chloride dihydrate, $CaCl_2 \cdot 2H_2O$.

A.4.2 Calcium chloride solution, $\rho(Ca^{2+})$, approximately 10 g/l.

Dissolve 3,7 g calcium chloride dihydrate (A.4.1) in approximately 80 ml water (6.1) in a 100 ml volumetric flask and dilute to volume with water (6.1).

A.5 Apparatus

See Clause 7 and the following.

A.5.1 Cartridges.

A.5.1.1 Cation exchanger in the H-form (cartridge).

A.5.1.2 Cation exchanger in the Ag-form (cartridge).

A.5.1.3 Cation exchanger in the Ba-form (cartridge).

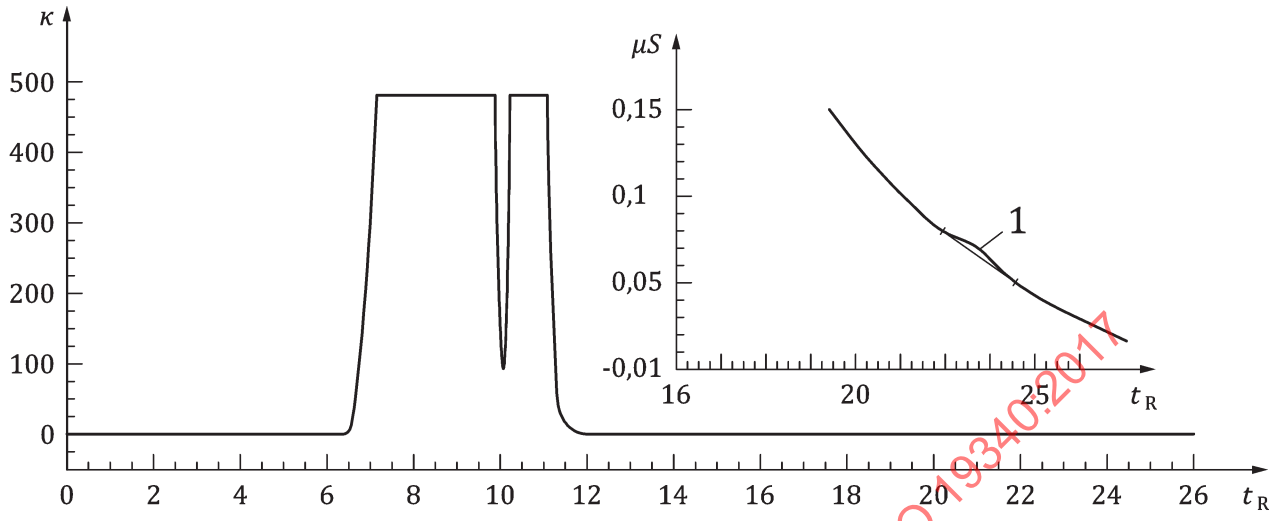
A.6 Quality requirements

See Clause 8 and the following.

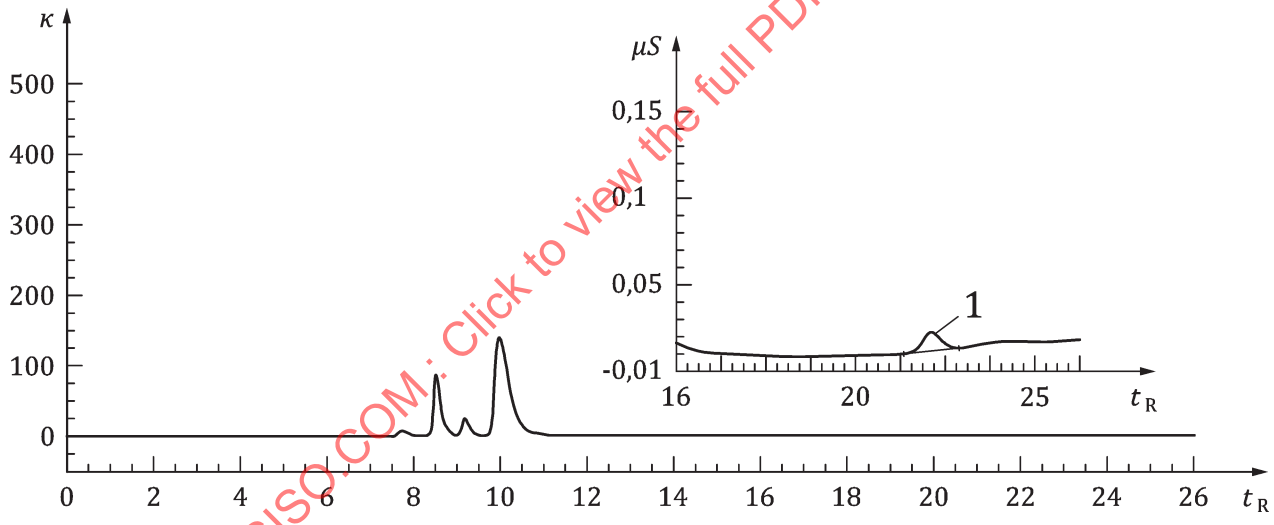
Figure A.1 gives an example for the separation of perchlorate applying cation exchanged SPE-cartridges.

Conditions for the chromatogram are shown in Figure A.1.

Sample:	River water, spiked with 3 µg/l ClO_4^- (matrix: 660 mg/l chloride, 260 mg/l sulfate, 14 mg/l nitrate)
Column:	Ion exchanger, 2 mm × 250 mm format
Eluent:	35 mmol/l KOH
Sample injection volume:	750 µl
Eluent flow rate:	0,25 ml/min
Detection:	Suppressed CD
Column oven temperature:	30 °C



a) Untreated sample



b) Treated sample

Key

1 perchlorate

t_R retention time, min

κ conductivity, µS/cm

Figure A.1 — Example of a chromatogram of untreated and treated samples

A.7 Procedure

A.7.1 Sample preparation

See Clause 9 and the following.

Remove chloride, sulfate, carbonate and hydrogen carbonate using ion exchange cartridges (A.5.1) (see Reference [8]).

Consider applying the following when using ion exchange cartridges: Carry out the following elution steps with a constant flow rate of between 1 ml/min to 2 ml/min. In addition, purge the sample with an inert gas (e.g. nitrogen or helium) to eliminate carbon dioxide (formed from carbonate and hydrogen carbonate salts), if necessary. The cartridges can be used for different samples as long as the chromatographic resolution, R, between perchlorate and its nearest peak does not fall below $R = 1{,}3$ (8.1).

Ba cartridges require the presence of Ca^{2+} or Mg^{2+} ions in the sample. The Ba ions of the respective resin need to be mobilized for the precipitation reaction with sulfate. This can happen either by calcium ions being present in the sample or, in case of low calcium containing sample, by a calcium chloride solution (A.4.2) added to the sample prior to the SPE-treatment. The chloride salt of the displacing calcium cation is used because the chloride counter ion can be trapped on the Ag-form resin. As long as the chromatographic resolution does not fall below $R = 1{,}3$ (8.1), a calcium chloride solution (A.4.2) need not be added.

Prepare the sample preparation cartridges (one each being Ba-loaded, Ag-loaded and in the H-form or a cartridge combining all three resins in one housing) according to the manufacturer's recommendation.

Connect the individual cartridges in order of Ba, Ag, H (Figure A.2) and rinse the cartridges with water (6.1) before use, according to the manufacturer's recommendation.

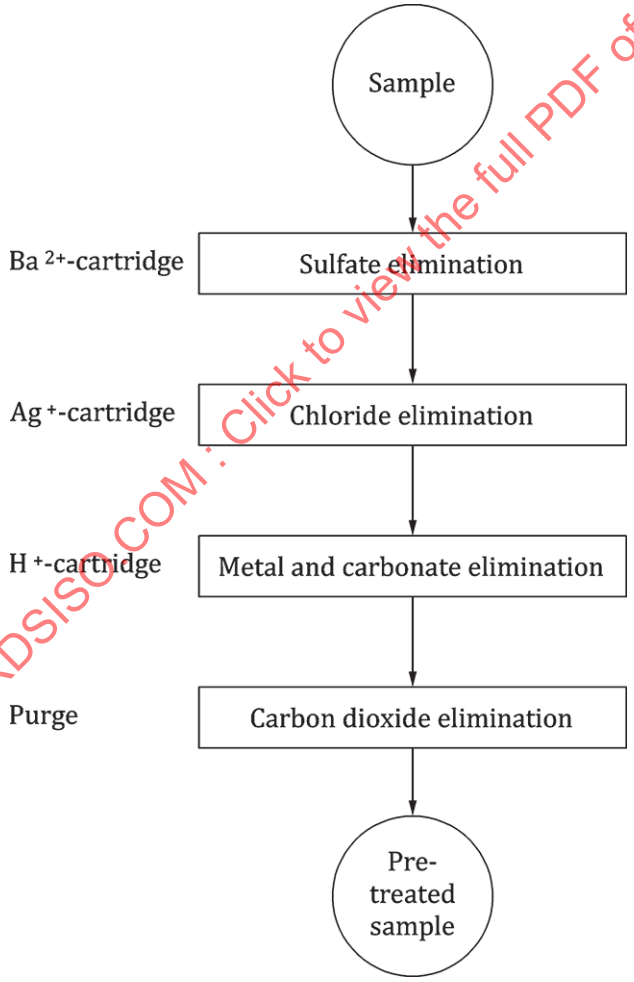


Figure A.2 — Pre-treatment steps for samples

Spike the sample with an appropriate amount of calcium, if necessary, e.g. adjust a concentration of 100 mg/l Ca^{2+}, dissolving 1 ml of the calcium chloride solution (A.4.2) in a 100 ml volumetric flask and dilute to volume with sample.

NOTE Ca^{2+}-concentrations below 100 mg/l can lead to an incomplete elimination of sulfate ions. It might be helpful to check the Ca^{2+} content of the sample before spiking additional calcium chloride to the sample as long as the resolution, *R*, falls below 1,3.

Apply the spiked sample to the cartridge train at less than 2 ml/min. Follow the manufacturer's recommendation, e.g. discard the first 3 ml for a 1,0 ml cartridge and 6 ml for a 2,5 ml cartridge.

A.7.2 Measurement of perchlorate

Measure the pre-treated samples as described in 10.3.

Figure A.1 shows a typical chromatogram of a real sample with and without SPE sample preparation.

Alternatively apply inline matrix elimination techniques according to Annex B or Annex C.

Annex B
(normative)

Determination of perchlorate using inline matrix elimination and applying re-injection analysis

B.1 General

This annex specifies the determination of perchlorate using an inline matrix elimination and application of the re-injection technique using a single eluent and a single separator column.

The requirements given in Clauses 1 to 13 remain valid.

B.2 Scope

See Clause 1 and the following.

This modification is applicable for samples with higher loads of dissolved salts (e.g. chloride, sulfate, carbonate) causing interference with the determination of perchlorate applying sample injection volumes up to 4 ml. The method is applicable for the determination of perchlorate concentrations ≥ 1 µg/l.

This modification utilizes inline techniques to reduce dissolved salts concentrations in the sample matrix and to collect perchlorate on a concentrator column or in a loop.

B.3 Principle

See Clause 5 and the following.

Decrease the dissolved salt concentrations using an inline matrix elimination step after having separated perchlorate from the major ions on the separator column.

A second injection valve is used for matrix elimination, collection and re-injection of perchlorate (Figure B.1; left injection valve).

Matrix elimination is done by diverting the volume of suppressed eluent collecting perchlorate on a concentrator or in a loop. The volume containing the matrix ions is directed to waste.

Elute the diverted eluent fraction from the concentrator or loop to the same separator column, where perchlorate is separated from the remaining anions and detected by suppressed conductivity.

B.4 Apparatus

See Clause 7 and the following.

In general, an ion chromatographic system including an inline matrix elimination system and applying re-injection analysis consists of the following components (see Figure B.1).

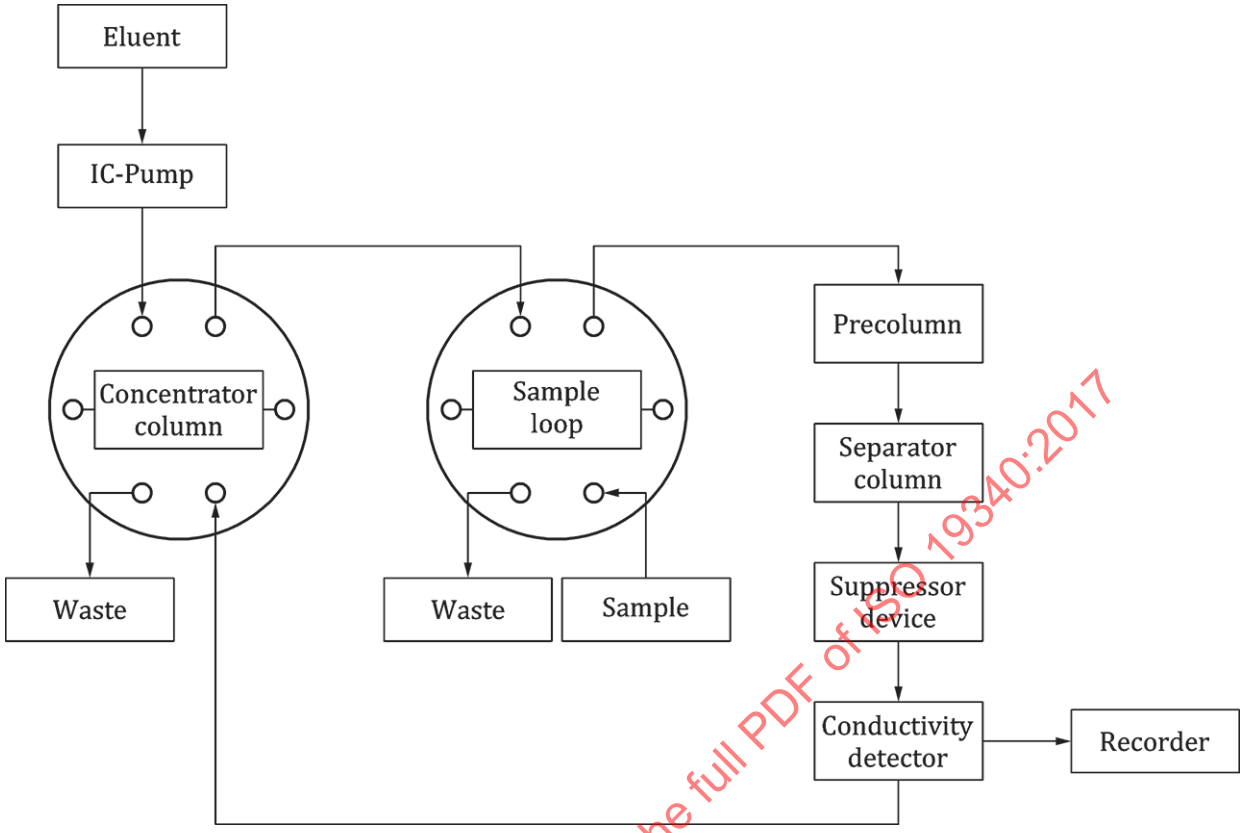


Figure B.1 — Schematic representation of an ion chromatographic system including an inline matrix elimination system and applying re-injection analysis

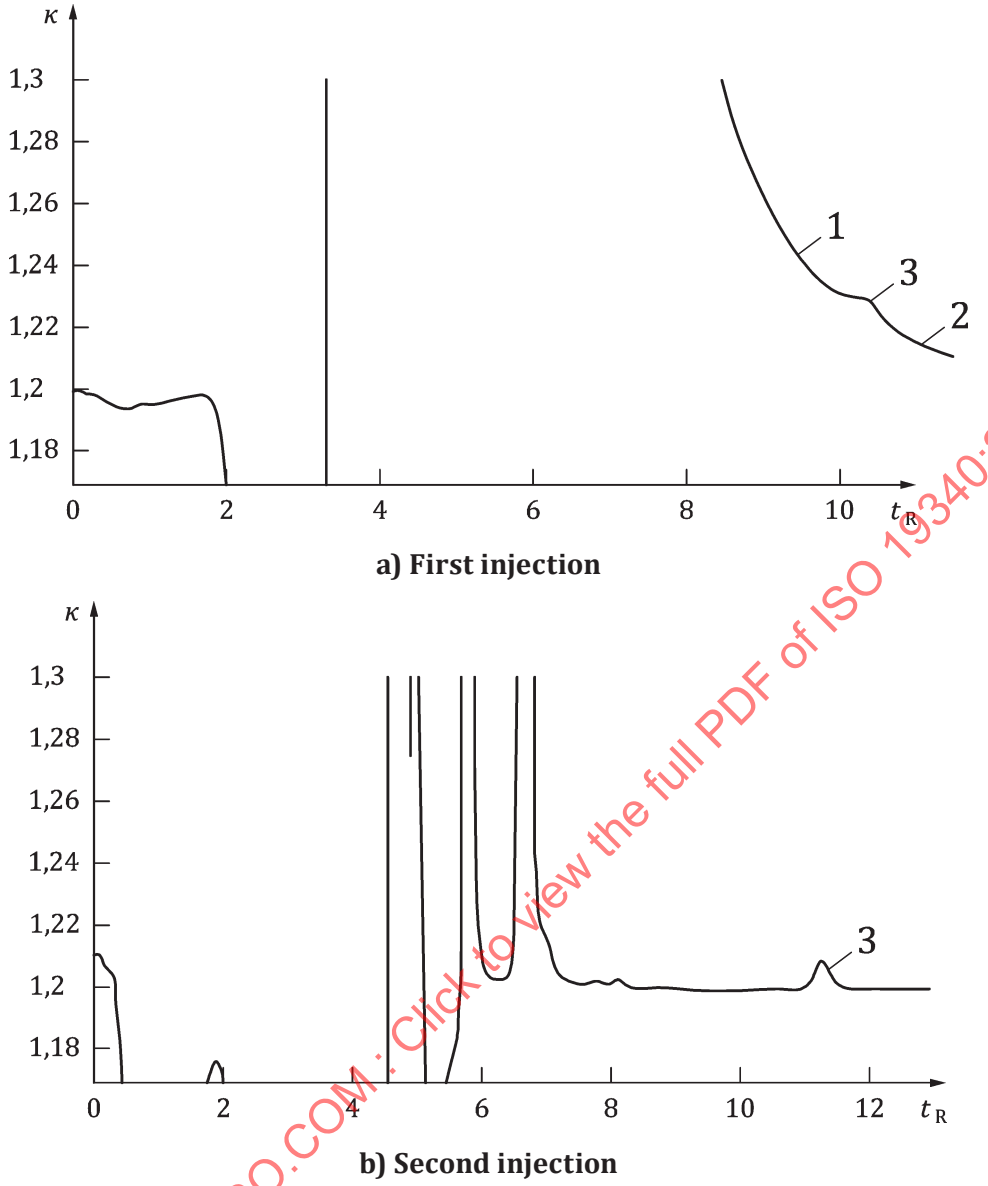
B.5 Quality requirements

See Clause 8 and the following.

Figure B.2 gives an example for the separation of perchlorate after matrix elimination.

Conditions for the chromatogram are shown in Figure B.2.

Sample:	Artificial ground water (matrix = 100 mg/l chloride, hydrogen carbonate, nitrate, sulfate) spiked with 2 µg/l ClO_4^-
Column:	Ion exchanger
Eluent:	10 mmol/l Na_2CO_3
Sample injection volume:	1 000 µl
Eluent flow rate:	0,8 ml/min
Detection:	CD
Column oven temperature:	60 °C



Key

t_R retention time, min
κ conductivity, µS/cm
1 begin of re-injection window
2 end of re-injection window
3 perchlorate

Figure B.2 — Example for a chromatogram of an artificial ground water sample using inline matrix elimination of perchlorate and applying re-injection analysis

B.6 Procedure

See Clause 10 and the following.

For validation of the procedural conditions, it is essential to determine the start and stop times of the re-injection window times for the primary column to ensure the best possible recovery of perchlorate. Carry out all of the procedural steps in accordance with the manufacturer's instructions. Analyse a calibration solution (e.g. 6.5) for the determination of the stop time of the re-injection window.

Alternatively apply matrix elimination techniques according to Annex A or Annex C.

Annex C
(normative)

Determination of perchlorate using inline matrix elimination and concentration applying two-dimensional ion chromatography (2DIC)

C.1 General

This annex specifies the determination of perchlorate using an inline matrix elimination and sample concentration step and applying two eluents of differing elution strength and two separation columns of identical or different selectivity and format.

The requirements given in Clauses 1 to 13 remain valid.

C.2 Scope

See Clause 1 and the following.

This modification is applicable for samples with higher loads of dissolved salts (e.g. chloride, sulfate, carbonate) causing interference with the determination of perchlorate applying sample injection volumes up to 4 ml. The method is applicable for the determination of perchlorate concentrations of ≥ 1 µg/l.

This modification utilizes inline techniques to decrease dissolved salts concentrations in the sample matrix and collects perchlorate on an inline concentrator device (e.g. column) or in a loop applying two separator columns of identical or different selectivity (heart-cutting).

C.3 Principle

See Clause 5 and the following.

Decrease the dissolved salt concentrations using an inline matrix elimination step after having perchlorate separated.

Matrix elimination is achieved by diverting the volume of suppressed eluent containing perchlorate to a concentrator or loop. The volume containing the matrix ions is directed to waste.

The diverted eluent fraction is transferred from the concentrator column or the loop onto a second separator column, where perchlorate is separated from the remaining anions and detected by suppressed conductivity. A concentration step is achieved by using a second column with a smaller inner diameter compared to the first column.

C.4 Reagents

See Clause 6.

C.5 Apparatus

See Clause 7 and the following

C.5.1 Second pump.

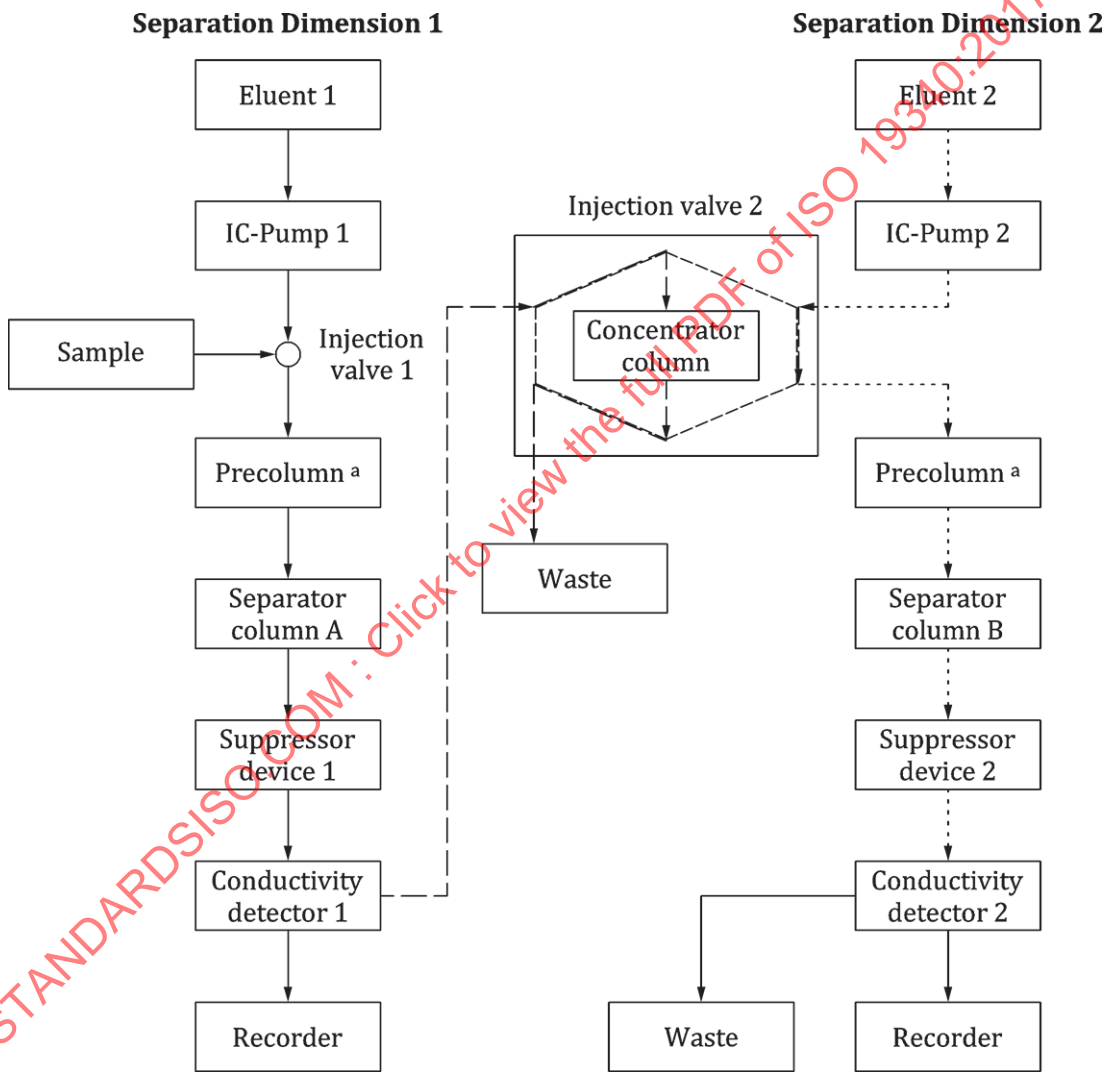
C.5.2 Second injection valve (used for matrix elimination).

C.5.3 Set of two column sets with identical or different selectivity or format.

C.5.4 Second suppressor.

C.5.5 Second conductivity detector.

In general, a 2DIC system consists of the following components (see Figure C.1).



Key

——— separation of matrix from analytes

— — — concentration of perchlorate followed by separation in dimension 1

..... separation of perchlorate in dimension 2

a Optional.

Figure C.1 — Schematic representation of a two-dimensional ion chromatographic system (2DIC) including inline matrix elimination, analyte concentration and two separator columns with different selectivity or formats

C.6 Quality requirements

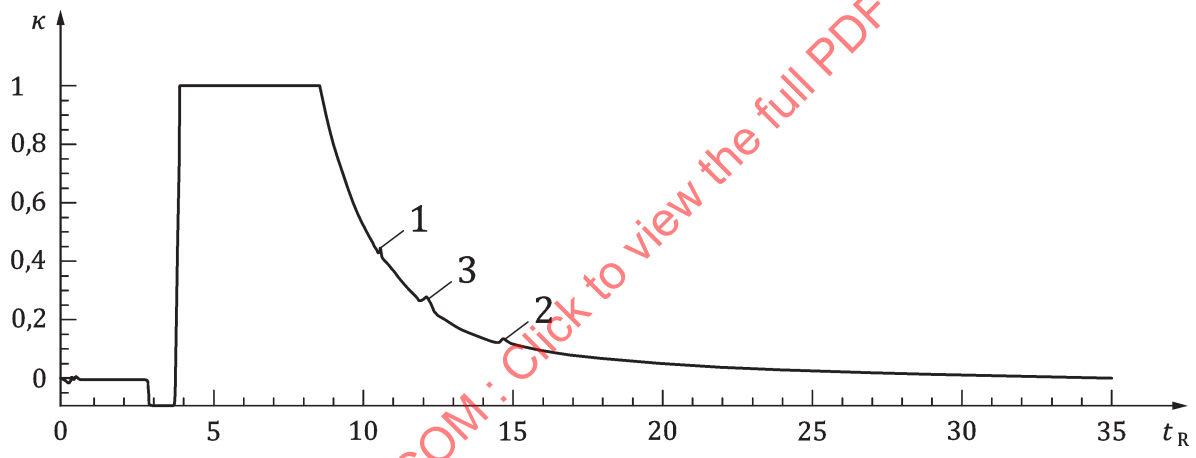
See Clause 8 and the following.

Figure C.2 gives an example for the separation of perchlorate applying 2DIC.

Conditions for the chromatogram are shown in Figure C.2.

First dimension

Sample:	Ground water containing 5,6 µg/l ClO_4^-
Column/column temperature:	Ion exchanger of Type A (4 mm × 250 mm) at 30 °C
Eluent:	40 mmol/l KOH
Sample injection volume:	1 000 µl
Eluent flow rate:	1 ml/min
Detection:	CD



a) First dimension