BRITISH STANDARD

BS EN ISO 15061:2001

BS 6068-2.73: 2001

Water quality — Determination of dissolved bromate — Method by liquid chromatography of ions

The European Standard EN ISO 15061:2001 has the status of a British Standard

ICS 13.060.01

Confirmed
July 2008

National foreword

This British Standard is the official English language version of EN ISO 15061:2001. It is identical with ISO 15061:2001.

The UK participation in its preparation was entrusted by Technical Committee EH/3, Water quality, to Subcommittee EH/3/2, Physical, chemical and biochemical methods, which has the responsibility to:

- aid enquirers to understand the text;
- present to the responsible international/European committee any enquiries on the interpretation, or proposals for change, and keep the UK interests informed;
- monitor related international and European developments and promulgate them in the UK.

A list of organizations represented on this committee can be obtained on request to its secretary.

BS EN ISO 15061 is one of a series of standards on water quality, others of which have been, or will be, published as Sections of BS 6068. This standard has therefore been given the secondary identifier BS 6068-2.73. The various Sections of BS 6068 are comprised within Parts 1 to 7, which, together with Part 0, are listed below.

Part 0 *Introduction*
Part 1 *Glossary*
Part 2 *Physical, chemical and biochemical methods*
Part 3 *Radiological methods*
Part 4 *Microbiological methods*
Part 5 *Biological methods*
Part 6 *Sampling*
Part 7 *Precision and accuracy*

NOTE. The test described in this British Standard should only be carried out by suitably qualified persons with an appropriate level of chemical expertise. Standard chemical procedure should be followed through.

Cross-references

The British Standards which implement international or European publications referred to in this document may be found in the BSI Standards Catalogue under the section entitled "International Standards Correspondence Index", or by using the "Find" facility of the BSI Standards Electronic Catalogue.

This British Standard, having been prepared under the direction of the Health and Environmental Sector Committee, was published under the authority of the Standards Committee and comes into effect on 15 September 2001

Summary of pages

This document comprises a front cover, an inside front cover, the EN ISO title page, the EN ISO foreword page, the ISO title page, pages ii to v, a blank page, pages 1 to 21, and a back cover.

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EUROPEAN STANDARD
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EN ISO 15061

July 2001

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English version

Water quality - Determination of dissolved bromate - Method by liquid chromatography of ions (ISO 15061:2001)

Qualité de l'eau - Dosage du bromate dissous - Méthode par chromatographie des ions en phase liquide (ISO 15061:2001)

Wasserbeschaffenheit - Bestimmung von gelöstem Bromat - Verfahren mittels Ionenchromatographie (ISO 15061:2001)

This European Standard was approved by CEN on 28 June 2001.

CEN members are bound to comply with the CEN/CENELEC Internal Regulations which stipulate the conditions for giving this European Standard the status of a national standard without any alteration. Up-to-date lists and bibliographical references concerning such national standards may be obtained on application to the Management Centre or to any CEN member.

This European Standard exists in three official versions (English, French, German). A version in any other language made by translation under the responsibility of a CEN member into its own language and notified to the Management Centre has the same status as the official versions.

CEN members are the national standards bodies of Austria, Belgium, Czech Republic, Denmark, Finland, France, Germany, Greece, Iceland, Ireland, Italy, Luxembourg, Netherlands, Norway, Portugal, Spain, Sweden, Switzerland and United Kingdom.

EUROPEAN COMMITTEE FOR STANDARDIZATION
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EUROPÄISCHES KOMITEE FÜR NORMUNG

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Ref. No. EN ISO 15061:2001 E

Foreword

The text of the International Standard ISO 15061:2001 has been prepared by Technical Committee ISO/TC 147 "Water quality" in collaboration with Technical Committee CEN/TC 230 "Water analysis", the secretariat of which is held by DIN.

This European Standard shall be given the status of a national standard, either by publication of an identical text or by endorsement, at the latest by January 2002, and conflicting national standards shall be withdrawn at the latest by January 2002.

According to the CEN/CENELEC Internal Regulations, the national standards organizations of the following countries are bound to implement this European Standard: Austria, Belgium, Czech Republic, Denmark, Finland, France, Germany, Greece, Iceland, Ireland, Italy, Luxembourg, Netherlands, Norway, Portugal, Spain, Sweden, Switzerland and the United Kingdom.

NOTE FROM CMC: The foreword is susceptible to be amended on reception of the German language version. The confirmed or amended foreword, and when appropriate, the normative annex ZA for the references to international publications with their relevant European publications will be circulated with the German version.

Endorsement notice

The text of the International Standard ISO 15061:2001 was approved by CEN as a European Standard without any modification.

INTERNATIONAL STANDARD

ISO
15061

First edition
2001-07-01

Water quality — Determination of dissolved bromate — Method by liquid chromatography of ions

Qualité de l'eau — Dosage du bromate dissous — Méthode par chromatographie des ions en phase liquide

Reference number
ISO 15061:2001(E)

Contents

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.

International Standards are drafted in accordance with the rules given in the ISO/IEC Directives, Part 3.

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.

Attention is drawn to the possibility that some of the elements of this International Standard may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights.

International Standard ISO 15061 was prepared by Technical Committee ISO/TC 147, *Water quality*, Subcommittee SC 2, *Physical, chemical and biochemical methods*.

Annexes A, B, C, D and E of this International Standard are for information only.

Introduction

The essential minimum requirements of an ion chromatographic system applied within the scope of this International Standard for the determination of dissolved bromate are given in clause 5.

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

Further information on the analytical technique can be found in the normative references (clause 2) and the bibliography.

Water quality — Determination of dissolved bromate — Method by liquid chromatography of ions

1 Scope

This International Standard specifies a method for the determination of dissolved bromate in water (e.g. drinking water, raw water, surface water, partially treated water or swimming pool water).

Appropriate pretreatment of the sample, for example by elimination of chloride, sulfate, metals, preconcentration or dilution, gives a range of applicability of 0,5 µg/l to 1 000 µg/l dissolved bromate.

The working range is restricted by the ion-exchange capacity of any preconcentration columns used and that of the separator column. Dilution of the sample to the working range may be necessary.

2 Normative references

The following normative documents contain provisions which, through reference in this text, constitute provisions of this International Standard. For dated references, subsequent amendments to, or revisions of, any of these publications do not apply. However, parties to agreements based on this International Standard are encouraged to investigate the possibility of applying the most recent editions of the normative documents indicated below. For undated references, the latest edition of the normative document referred to applies. Members of ISO and IEC maintain registers of currently valid International Standards.

ISO 3696:1987, *Water for analytical laboratory use — Specification and test methods.*

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 8466-2:1993, *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 Interferences

3.1 The presence of nitrate, chloride, carbonate and sulfate may affect the capacity of the concentrator column and lead to poor recovery of bromate (9.2.1).

3.2 The presence of chloride, sulfate, carbonate and hydrogen carbonate can cause interference with the determination of bromate (9.2.1). Depending on the column utilized, other ions may interfere; this should be checked.

3.3 Metals present (e.g. barium and silver ions released from sample pretreatment steps) will bind to the resin material of concentrator and separator columns, resulting in a loss of performance. Metal ions may be eliminated with the aid of a metal clean-up column or special exchangers (see Figure 1 and clause 9).

3.4 The interference of some organic acids with the determination of bromate was checked and found not to be significant to the concentrations tested (annex E).

3.5 Solid particles and organic compounds such as mineral oils, detergents and humic acids shorten the life-time of the concentrator and separator column.

4 Principle

4.1 Sample pretreatment is carried out in order to remove ozone (9.1.3) and solids, and to reduce chloride, sulfate, carbonate, hydrogen carbonate and metals present by use of cation exchangers (9.2).

4.2 Measurement of bromate is made in the range 0,5 µg/l to 1 000 µg/l, with or without preconcentration (10.3).

4.3 Liquid chromatographic separation of bromate is carried out either by means of a separator column or after elution of bromate from a concentrator column, if used. An anion exchange resin is used as the stationary phase, and usually, aqueous solutions of salts of weak mono- and dibasic acids as eluent (see 6.10 and annex A).

4.4 A conductivity detector (CD) with chemical suppression is used. A UV detector ($\lambda = 190$ nm to 205 nm) is suitable to confirm the CD results only.

NOTE When using conductivity detectors it is essential that the eluents have a sufficiently low conductivity. For this reason, conductivity detectors are combined with a suppressor device (cation exchanger) which reduces the conductivity of the eluent and transforms the sample species into their respective acids. UV detection measures absorbance directly.

4.5 Strongly retained ions (e.g. nitrate, phosphate, sulfate) are removed from the separator column, e.g. by flushing the separator column with a more concentrated eluent.

4.6 The concentration of bromate is determined after calibration of the overall procedure.

5 Essential minimum requirements

a) Preconcentration

For low bromate concentrations the use of a concentrator column may be required. On-line techniques can be used (see 10.3 and annex C). Ensure that recovery is within 80 % to 120 %.

b) Resolution power of the column

It is essential that the peak resolution R shall not fall below 1,3 (clause 8, Figure 4) between bromate and the nearest peak, which is usually chloride.

c) Method of detection

Measurement of the electrical conductivity (CD) with a chemical suppressor device, and UV if confirmation is required.

d) Applicability of the method: 0,5 µg/l to 1 000 µg/l.

e) Calibration shall be carried out in accordance with ISO 8466-1 or ISO 8466-2 (10.2).

f) Guarantee of analytical quality

Control is necessary for the validity of the calibration function (10.5). Replicate determinations may be necessary. Use of the method of standard addition may be required when matrix interferences are expected (10.3).

6 Reagents

Use only reagents of recognized analytical grade. Carry out weighing of the reagents with an accuracy of ± 1 % of the nominal mass, unless stated otherwise.

6.1 Water, complying with grade 1 as defined in ISO 3696.

6.2 Sodium hydrogen carbonate, $NaHCO_3$.

6.3 Sodium carbonate, Na_2CO_3.

6.4 Disodium tetraborate decahydrate, $Na_2B_4O_7 \cdot 10\ H_2O$.

6.5 Boric acid, H_3BO_3.

6.6 Potassium bromate, $KBrO_3$.

6.7 Nitric acid, $c(HNO_3) = 0{,}1$ mol/l.

6.8 Sulfuric acid, $\rho(H_2SO_4) = 1{,}84$ g/ml.

6.9 Ethylenediamine, $C_2H_8N_2$.

6.10 Eluents.

Degas all water used for eluent preparation. 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.

See annex A for examples of eluents.

Two different types of eluent are used.

6.10.1 Eluent of Type 1, of a lower concentration level (for examples see clause A.1) to be applicable for the separation of bromate

and

6.10.2 Eluent of Type 2, of a higher concentration level (for examples see clause A.2) to be applicable to remove strongly retained ions (e.g. nitrate, phosphate) from the concentrator and separator column.

The choice of eluent is dependent on the choice of column and detector; seek advice from the column supplier. The chosen combination of separator column and eluent shall conform to the resolution requirements stated in clause 8.

A selection of reagents for common eluents is presented in 6.2 to 6.5.

6.11 Bromate stock standard solution, $\rho(BrO_3^-) = 1\ 000$ mg/l

Dry approximately 1,5 g of potassium bromate (6.6) for at least 1 h at 105 °C ± 5 °C. Store the dried solid in a desiccator.

Dissolve 1,306 g ± 0,001 g of the dried potassium bromate 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 6 °C in polyethylene or glass bottles and renew it every 12 months.

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

6.12 Bromate standard solutions.

6.12.1 General

Depending upon the concentrations expected, prepare the following standard solutions of different bromate concentrations from the stock standard solution (6.11). Note the possible risk of changes in concentration caused by interaction with the vessel material increases with decreasing bromate concentration. Store the standard solutions in polyethylene or glass bottles.

6.12.2 Bromate Standard Solution I

The mass concentration of this solution is $\rho(BrO_3^-) = 100$ mg/l.

Pipette 10,0 ml of stock standard solution (6.11) into a 100 ml volumetric flask, and dilute to volume with water (6.1).

Store the solution at 2 °C to 6 °C in polyethylene or glass bottles and renew every 6 months.

6.12.3 Bromate Standard Solution II

The mass concentration of this solution is $\rho(BrO_3^-) = 1$ mg/l.

Pipette 1,0 ml of Standard Solution I (6.12.2) into a 100 ml volumetric flask, dilute to volume with water (6.1).

Store the solution at 2 °C to 6 °C in polyethylene or glass bottles and renew every 3 months.

6.13 Bromate calibration solutions.

Depending on the bromate concentration expected in the sample, use the Bromate Standard Solution I or II (6.12.2 or 6.12.3) to prepare five to ten calibration solutions distributed over the expected working range as evenly as possible.

For example, proceed as follows for the range 0,5 µg/l to 5,0 µg/l BrO_3^-:

Pipette, into a series of 100 ml volumetric flasks, the following volumes: 50 µl, 100 µl, 150 µl, 200 µl, 250 µl, 300 µl, 350 µl, 400 µl, 450 µl or 500 µl of Bromate Standard Solution II (6.12.3) and dilute to volume with water (6.1).

The concentrations of BrO_3^- in these calibration solutions are: 0,5 µg/l, 1,0 µg/l, 1,5 µg/l, 2,0 µg/l, 2,5 µg/l, 3,0 µg/l, 3,5 µg/l, 4,0 µg/l, 4,5 µg/l and 5,0 µg/l respectively.

Prepare the calibration solutions on the day of use.

6.14 Regeneration solutions.

The choice is dependent on the type of metal clean-up columns or suppressor devices. Therefore, follow the column manufacturer's instructions for the exact composition of the regeneration solutions (for examples of compositions see annex B).

6.15 Blank solution.

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

7 Apparatus

Usual laboratory apparatus, and, in particular:

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

a) eluent reservoirs, and a degassing unit for two eluents;

b) pump, suitable for step gradient technique;

c) sample delivery device (e.g. sample pump) including a sample injection system incorporating a sample loop of appropriate volume (e.g. 0,05 ml to 2 ml) or autosampler device;

d) column-switching valves (e.g. 6-port-valve) including a device for timing and controlling valves and pump;

e) concentrator column (may be required for low concentrations);

f) separator column with the specified separating performance (see clause 8);

g) conductivity detector with an anion suppressor device assembly;

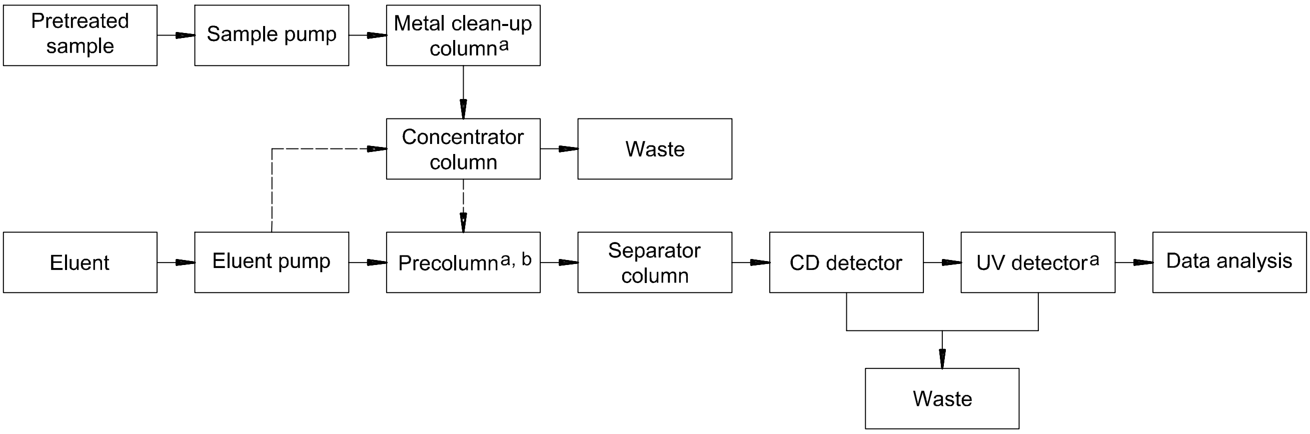
h) UV detector (e.g. spectrophotometer: 190 nm to 400 nm);

i) recording device (e.g. recorder, integrator with printer, PC with software for data acquisition and evaluation).

NOTE If a preconcentration step is required, see annex C for an example of a possible system configuration.

7.2 Cartridges.

- cation exchanger in the Ag-form (cartridge);
- cation exchanger in the Ba-form (cartridge);
- cation exchanger in the H-form (cartridge);
- optional: metal clean-up column for on-line use;
- cartridges with non-polar phases to be used for sample preparation (e.g. polyvinylpyrrolidone).



Key

[a] Optional.

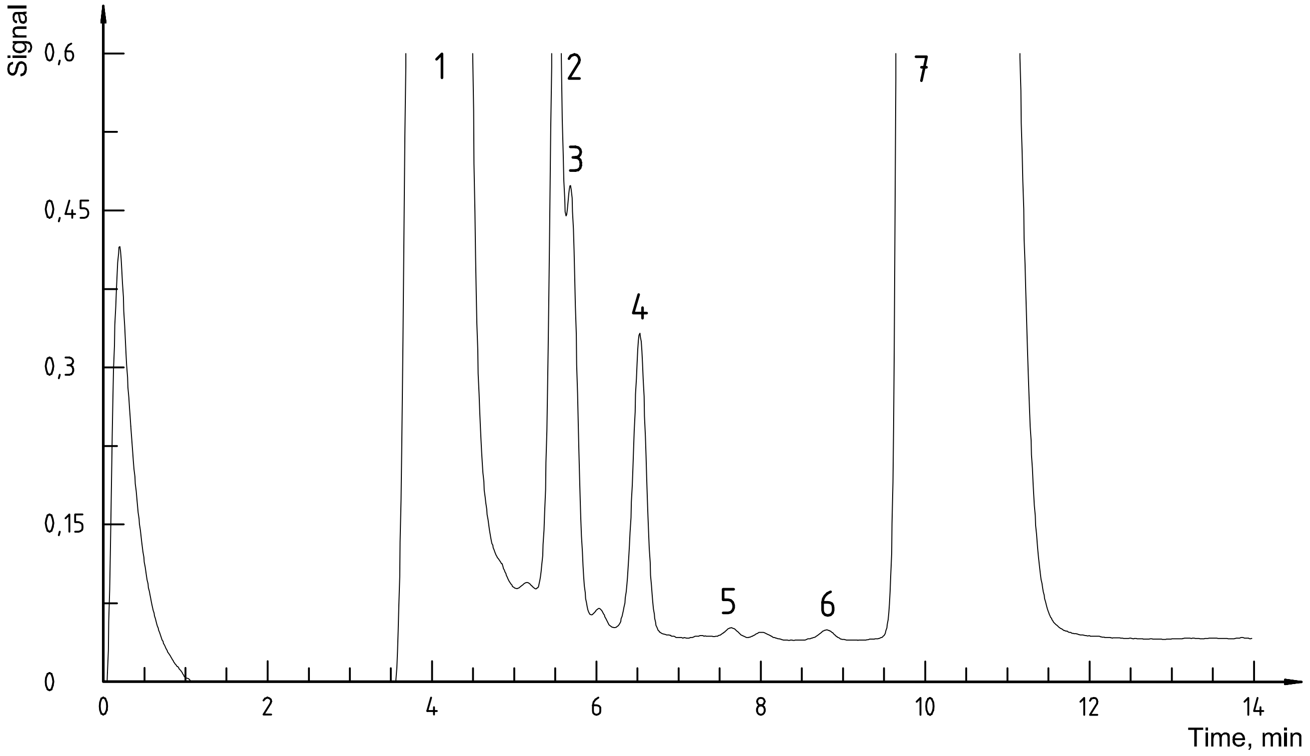
[b] To be recommended for direct injection, when not using a concentrator column (see 10.3, note 1).

Figure 1 — Schematic representation of an ion chromatographic system, including an on-line preconcentration system

8 Quality requirements for the separator column

Separation conditions shall be such that possible interfering anions do not interfere with bromate. Figures 2 and 3 give examples for different types of water matrix checked.

In chromatograms of samples and standard solutions of bromate, the peak resolution R between bromate and its nearest peak, usually chloride, shall not fall below 1,3 [see equation (1) and Figure 4].



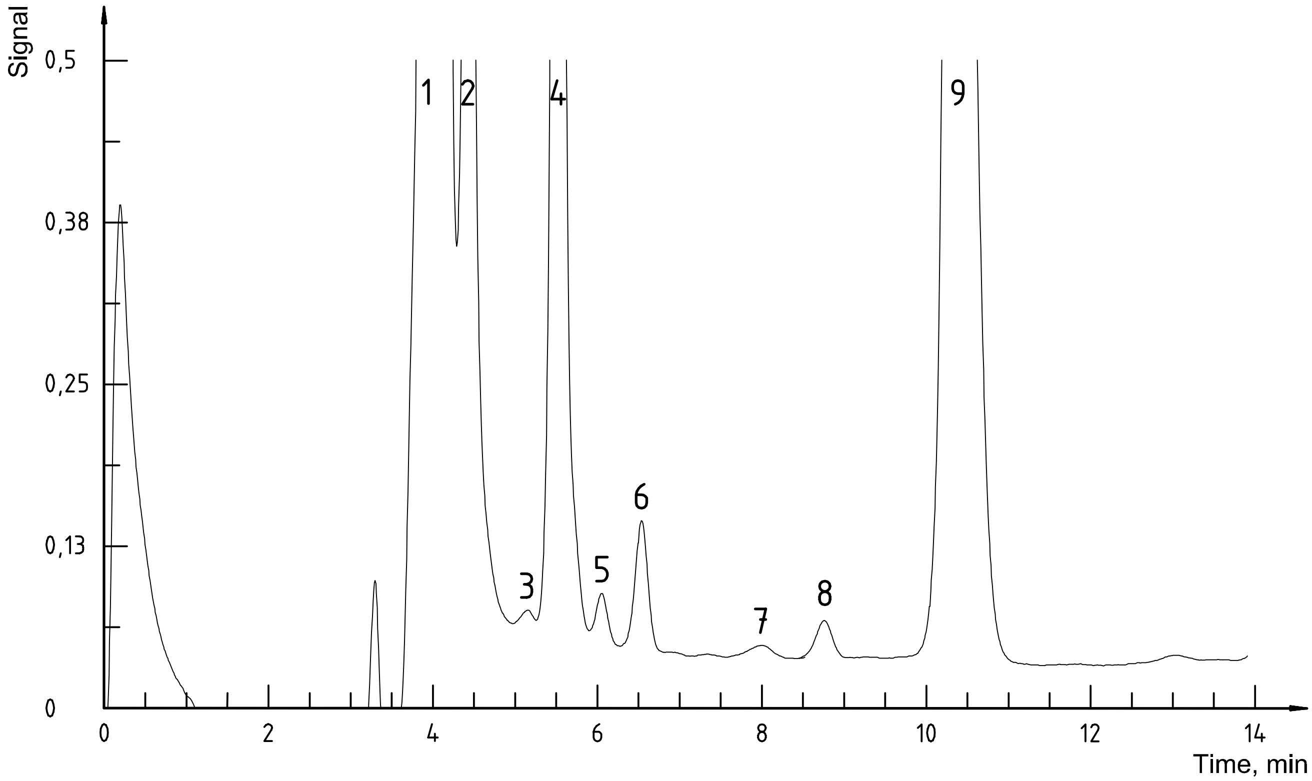
Key

1	Formate, lactate, propionate, acetate or butyrate	5	Monobromoacetate
2	Valerate or unknown	6	0,8 µg/l bromate
3	Unknown	7	Chloride
4	Chlorite		

NOTE 1 Verified identification of peaks 6 and 7. Uncertain identification of the other peaks.

NOTE 2 Sample preparation: preconcentration of 2 ml of sample after use of Ag- and H-cartridges according to 9.1.

Figure 2 — Example chromatogram of an ozonylated treated raw water sample prepared conforming to this International Standard



Key

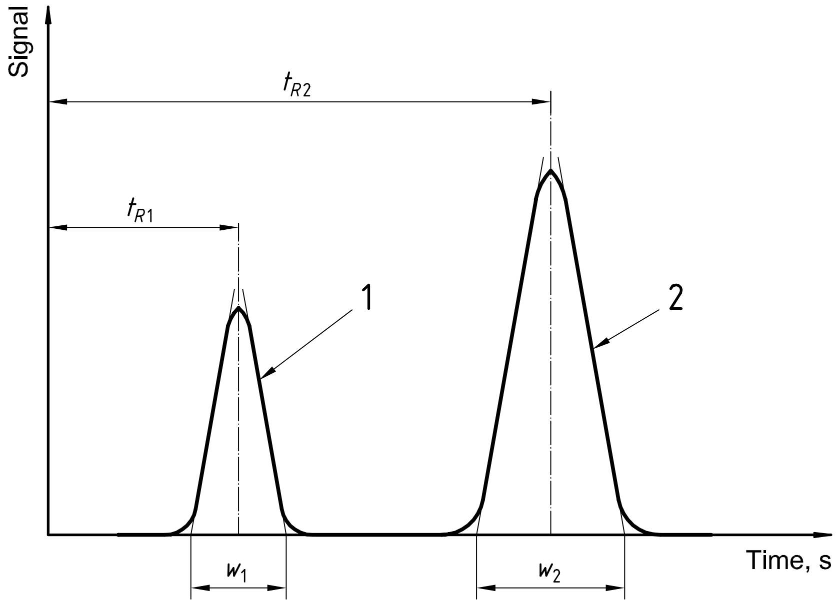
1	Formate
2	Propionate, acetate, or butyrate
3	Valerate
4	Unknown
5	Unknown
6	Chlorite
7	Unknown
8	Bromate
9	Chloride

NOTE 1 Verified identification of peaks 8 and 9. Uncertain identification of the other peaks.

NOTE 2 Sample preparation: preconcentration of 2 ml of sample after use of Ag- and H-cartridges according to 9.1.

NOTE 3 Elution sequences and retention times (t_R) can vary, depending on the type of column and the eluent composition.

Figure 3 — Chromatogram of a river sample (River Meuse, sample spiked with 3 µg/l bromate) prepared conforming to this International Standard



Key

1 Peak 1

2 Peak 2

Figure 4 — Graphical representation of the parameters to calculate the peak resolution R

Calculate the peak resolution R using equation (1):

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

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 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 w_1, w_2 are the base widths of the isosceles triangles constructed over the Gaussian peaks.

9 Sampling and sample pretreatment

9.1 General requirements

9.1.1 Sampling and sampling preservation procedures shall be in accordance with ISO 5667-1, ISO 5667-2 and ISO 5667-3. Treat the calibration solutions (6.13) and the blank solution (6.15) in the same manner as the sample solution (see Figure 5, steps 1 to 5 and 9.1.3 to 9.2.6).

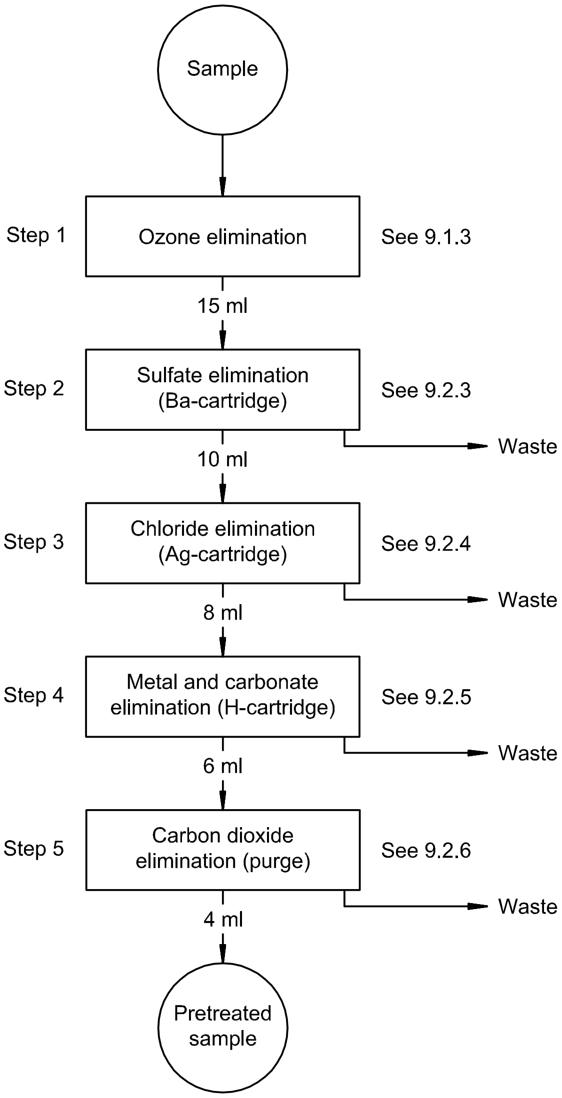


Figure 5 — Pretreatment steps for samples, calibration and blank solution

9.1.2 Use clean polyethylene vessels for sampling.

9.1.3 Avoid any further formation of bromate after sampling by immediately removing any ozone present. For example, add 50 mg of ethylenediamine (6.9) to 1 l of sample immediately after sampling (see Figure 5, step 1).

9.1.4 Store the sample in a polyethene vessel at 2 °C to 6 °C until analysis is carried out.

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

9.2.1 If considered necessary, remove chloride, sulfate, carbonate and hydrogen carbonate with the aid of the ion-exchange cartridges described, by carrying out the following elution steps with a constant flowrate of between 1 ml/min and 1,5 ml/min (see Figure 5, steps 2 to 4). Rinse ion-exchange cartridges with water (6.1) before use according to the manufacturer's instructions. In addition, purge the sample with an inert gas (e.g. N_2 or He) to eliminate carbon dioxide (formed from carbonate and hydrogen carbonate salts).

The presence of nitrate, chloride, carbonate and sulfate may affect the capacity of the concentrator column and may lead to poor recovery of bromate. This effect should be checked for every matrix by standard addition, and the recovery of bromate should be in the range 80 % to 120 %.

9.2.2 Prepare the samples as described in 9.1.

9.2.3 Pass approximately 15 ml of the sample through a cation exchanger in the Ba-form (cartridge, 7.2) to remove dissolved sulfate ions from the sample (see Figure 5, step 2). Discard the first portion of 2 ml.

9.2.4 Pass approximately 10 ml of the remaining sample through a strongly acid cation exchanger in the Ag-form (cartridge, 7.2) to remove dissolved halides from the sample (see Figure 5, step 3). Discard the first portion of 2 ml.

9.2.5 Pass approximately 8 ml of the remaining sample through a cation exchanger in the H-form (cartridge, 7.2) to remove dissolved metal ions, carbonate and hydrogen carbonate from the sample (see Figure 5, step 4). Discard the first portion of 2 ml.

NOTE Alternatively, connect all the clean-up columns/cartridges (see Figure 5, steps 2 to 4). In this case, the first 3 ml of eluate of the sample leaving the last cartridge should be discarded (see Figure 5, step 4).

9.2.6 Purge the remaining sample for approximately 5 min with an inert gas (e.g. N_2, He) in order to eliminate carbon dioxide from the sample (see Figure 5, step 5), and analyse the resulting eluate of the sample using the ion chromatographic system.

10 Procedure

10.1 General

Set up the ion chromatographic system (7.1) according to the instrument manufacturer's instructions.

Run the starting eluent; once the baseline is stable analysis can begin.

If metal clean-up, concentrator columns and suppressor devices are being used, regenerate according to the instrument manufacturer's instructions before use.

Perform the calibration as described in 10.2. Measure the samples and blank solution (6.15) as described in 10.3.

10.2 Calibration

Inject the pretreated bromate calibration solutions (6.13 and clause 9). In calculating concentrations, use the characteristic that the area (or height) of the peak (signal) is proportional to the concentration of the bromate ion.

When the analytical system is first evaluated, and at intervals afterwards, establish a calibration function in accordance with ISO 8466-1 or ISO 8466-2 for the measurement as follows.

a) Prepare the bromate calibration solutions as described in 6.13 and clause 9.

b) Analyse the calibration solutions chromatographically.

c) Use the data obtained to calculate the regression line in accordance with ISO 8466-1 or ISO 8466-2.

d) Subsequently, verify the continuing validity of the established calibration function (10.5).

10.3 Measurement of bromate

After establishing the calibration function, inject the pretreated sample (clause 9) into the chromatograph and measure the peaks as described above (clause 10).

Identify the bromate peak by comparing the retention time with that of bromate in the standard solutions (6.12). Take into account the fact that the retention times can be dependent on concentration and matrix.

If a concentrator column is not used, the use of a precolumn is recommended, especially for the injection of waters strongly contaminated with organics (see 3.5 and Figure 1). It serves to protect the analytical separator column.

NOTE 1 In general, 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.

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

If the bromate concentration of the sample falls short of the calibration range, establish a separate calibration function for the lower working range, preconcentrate the bromate solution, if necessary, and analyse it.

NOTE 2 There are a number of available systems which can carry out a preconcentration step. The manufacturer's instructions for each system should be followed. Annex C contains an example of a possible system configuration.

If matrix interferences are expected, use 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 (6.15) in the same manner.

10.4 Confirmation of bromate results

If required, confirm bromate concentrations greater than 2 µg/l by UV detection (λ = 200 nm) as follows.

a) Calculate the bromate slopes of the CD (b_1) and the UV detector (b_2) from calibration experiments according to 10.2, and calculate factor B using equation (2).

$$B = \frac{b_1}{b_2} \tag{2}$$

where

b_1 is the slope of the calibration function for the CD detector, e.g. mm · l/mg; µV · s · l/mg;

b_2 is the slope of the calibration function for the UV detector, e.g. mm · l/mg; µV · s · l/mg.

b) Analyse a bromate calibration solution, e.g. ρ (BrO_3) = 10 µg/l.

c) Record the measured CD value (Y_1) and the measured UV value (Y_2) for bromate.

d) Calculate the ordinate intercept for CD (a_1) and UV (a_2) according to 10.2.

e) Calculate the response ratio r [see equation (3)]:

$$r = \left(\frac{Y_1 - a_1}{Y_2 - a_2} \right) \tag{3}$$

where

r is the response ratio;

Y_1 is the measured value (size of signal) for the CD detector, in terms of peak height or peak area, respectively in millimetres or microvolt seconds;

Y_2 is the measured value (size of signal) for the UV detector, in terms of peak height or peak area, respectively in millimetres or microvolt seconds;

a_1 is the ordinate intercept of the calibration function (calculated blank) for the CD detector, e.g. mm, µV · s (10.2);

a_2 is the ordinate intercept of the calibration function (calculated blank) for the UV detector, e.g. mm, µV · s (10.2).

r [see equation (3)] shall be in the range of $B \pm 10$ %. If r exceeds the range of 10 %:

- use the method of standard addition;
- calculate r again; if r still exceeds the range of $B \pm 10$ % then mark the result as “bromate not confirmed”.

10.5 Validity check of the calibration function

In order to verify the continuing validity of the calibration function, measure standard solutions of different bromate concentrations in the lower and upper thirds of the working range. Carry this out after the set-up procedure (see clause 10) and after each sample series at least, but in any case after 20 measurements. Recalibrate, if necessary.

11 Calculation

Calculate the mass concentration, ρ, in micrograms per litre, of bromate in the solution using the peak areas or peak heights (10.3) in accordance with ISO 8466-1 or ISO 8466-2.

Take into account all of the dilution steps.

12 Expression of results

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

EXAMPLES

Bromate (BrO_3^-)	5,1 µg/l
Bromate (BrO_3^-)	0,6 µg/l

13 Test report

The test report shall contain the following information:

a) a reference to this International Standard;

b) identity of the water sample;

c) expression of the results in accordance with clause 12;

d) description of sample pretreatment, if relevant;

e) any deviation from this method.

Annex A
(informative)

Eluents

A.1 Examples of eluents of Type 1 to be used for bromate separation

A.1.1 General

Solutions of sodium hydroxide and salt solutions of weakly dissociated acids, such as sodium carbonate/sodium hydrogen carbonate, sodium hydrogen carbonate and sodium tetraborate, can be used.

A.1.2 Sodium hydrogen carbonate concentrate I

The addition of the following eluent concentrate is appropriate for the eluent preparation (A.1.3):

Place 58,8 g of sodium hydrogen carbonate (see 6.2) into a 1 000 ml volumetric flask, dissolve in water (6.1) and dilute to volume with water (6.1).

The solution contains 0,7 mol/l of sodium hydrogen carbonate. This solution is stable for several months if stored at 2 °C to 6 °C.

A.1.3 Sodium hydrogen carbonate eluent I

The following eluent is applicable for the determination of bromate:

Pipette 5 ml of the concentrate (A.1.2) into a 5 000 ml volumetric flask and dilute to volume with water (6.1).

The solution contains 0,000 7 mol/l of sodium hydrogen carbonate. The solution should be renewed every 3 d.

A.1.4 Borate eluent I

The following eluent is applicable for the determination of bromate:

Place 76,3 g of disodium tetraborate decahydrate (6.4) into a 5 000 ml volumetric flask, dissolve in approximately 4 000 ml of water (6.1), and dilute to volume with water (6.1).

The solution contains 0,04 mol/l of disodium tetraborate. The solution should be renewed every 3 d.

A.2 Examples of eluents of Type 2 to be used to remove strongly retained ions

A.2.1 General

Solutions of sodium hydroxide and salt solutions of weakly dissociated acids, such as sodium carbonate/sodium hydrogen carbonate, sodium hydrogen carbonate and sodium tetraborate, can be used.

A.2.2 Sodium carbonate/sodium hydrogen carbonate concentrate II

The addition of the following eluent concentrate is appropriate for the eluent preparation (A.2.3).

Place 10,6 g of sodium carbonate (6.3) and 8,4 g of sodium hydrogen carbonate (6.2) into a 1 000 ml volumetric flask, dissolve in water (6.1) and dilute to volume with water (6.1).

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

A.2.3 Sodium carbonate/sodium hydrogen carbonate eluent II

The following eluent is applicable for the removal of strongly retained ions from the separator column.

Place 50 ml of the concentrate (A.2.2) into a 500 ml volumetric flask and dilute to volume with water (6.1).

The solution contains 0,01 mol/l of sodium carbonate and 0,01 mol/l of sodium hydrogen carbonate. The solution should be renewed every 3 d.

A.2.4 Borate eluent II

The following eluent is applicable for the removal of strongly retained ions from the separator column.

Place 477 g of disodium tetraborate decahydrate (6.4) into a 5 000 ml volumetric flask, dissolve in approximately 4 000 ml of water (6.1), and dilute to volume with water (6.1).

The solution contains 0,25 mol/l of disodium tetraborate. The solution should be renewed every 3 d.

Annex B
(informative)

Regeneration solutions

B.1 General

If metal clean-up columns and/or suppressor devices are used, these should be regenerated on a regular basis. The timing of the regeneration shall be determined for each system, and the following regenerant solutions may be used.

B.2 Example of a regenerant solution for metal clean-up columns

The use of nitric acid (6.7) is applicable for the regeneration of metal clean-up columns.

B.3 Example of a regenerant solution for suppressor devices

The use of sulfuric acid is applicable for the regeneration of suppressor devices.

Pipette 3,5 ml of sulfuric acid (6.8) into approximately 4 000 ml of water (6.1) in a 5 000 ml volumetric flask and dilute to volume with water (6.1).

The solution contains 0,012 6 mol/l of H_2SO_4 and is stable for several months if stored at $\leqslant 30$ °C.

Annex C
(informative)

Example of column-switching technique

C.1 General

Set up the ion chromatographic system in accordance with clause 10.

The manufacturer's instructions should always be followed. The times required for rinsing and equilibration of the system depend, e.g., on the properties of both the given ion-exchange column and the used eluent. Check these times experimentally. All times stated in C.2 to C.7 are intended as examples only. All valve and pump operations can be externally controlled by a time-sequence device (e.g. PC-based chromatography data station). Regenerate the metal clean-up column in accordance with the manufacturer´s instructions.

C.2 System set-up and load of the sample loop

Switch valve 1 (see Figure C.1) allowing the passage of water (6.1) through the metal clean-up column onto the concentrator column. Rinse the system with water (6.1). Fill the injection loop with the pretreated sample.

C.3 Sample injection and preconcentration

Inject 2 ml of the pretreated sample (9.2.6) via valve 1 (see Figure C.1) through the metal clean-up column onto the concentrator column.

C.4 Elution and separation of bromate

Switch valve 2 (see Figure C.1) into position so that eluent type 1 (see clause A.1) is pumped through the concentrator and the separator column.

C.5 Recording

Record the conductivity detector's output signal (e.g. peak area or height).

C.6 Reconditioning of columns

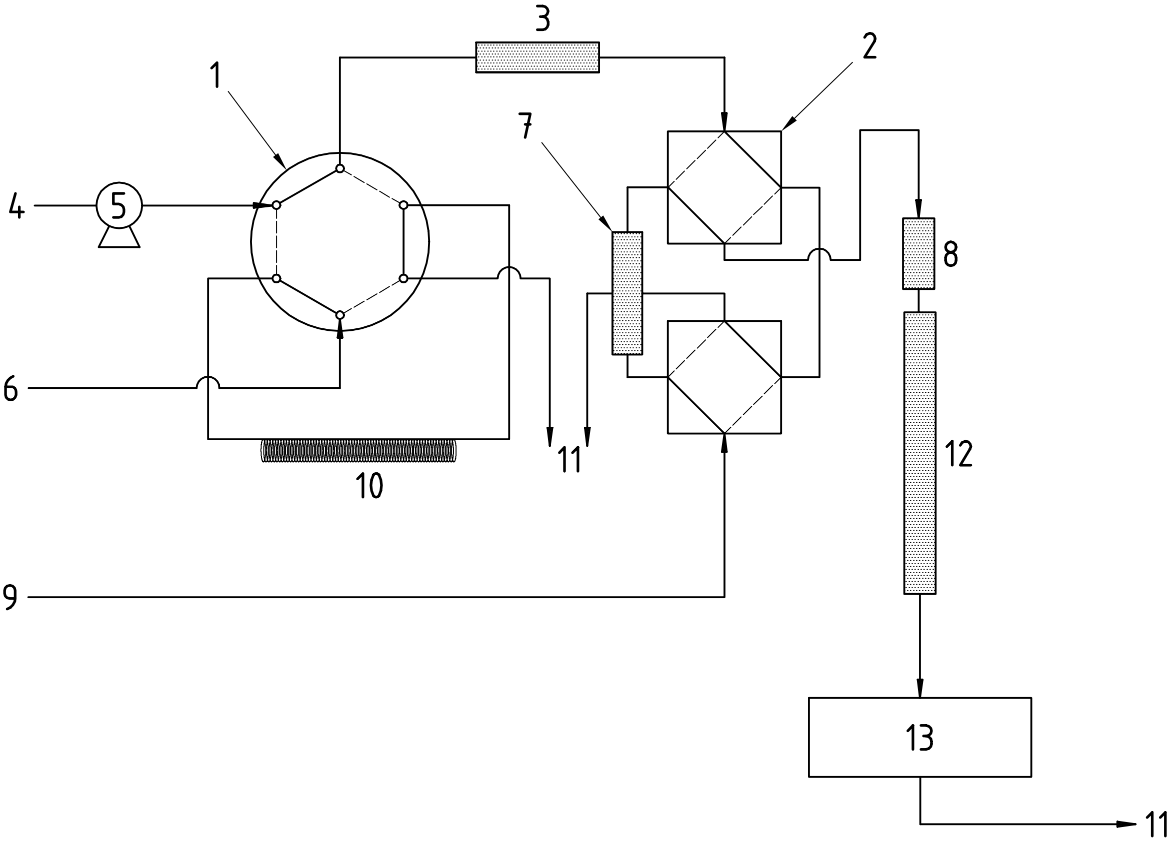
Deliver eluent type 2 (see clause A.2) using the analytical pump (see Figure C.1) through the concentrator and separator column. Rinse both columns for 5 min with eluent type 2 (see clause A.2).

C.7 Equilibration of the IC system

Using the chromatograph's pump (see Figure C.1), deliver eluent type 1 (see clause A.1) through concentrator and separator column. Rinse both columns for 5 min with eluent type 1 (see clause A.1). Equilibrate the ion chromatograph (clause 10) according to the instrument manufacturer's instructions (e.g. the instrument is ready for operation as soon as the baseline is stable).

C.8 Preparation of the next sample

Concentrate and measure the next sample in accordance with clauses C.1 to C.6.



Key

1	Valve 1: 6-Port injection valve	8	Precolumn
2	Valve 2: 8-Port column switch valve	9	Eluent
3	Metal clean-up column	10	2 ml injection loop
4	Water	11	Waste
5	Sample pump	12	Separator column
6	Pretreated sample	13	Suppressor CD detector
7	Concentrator column		

Figure C.1 — Example of an ion chromatographic system using the column-switching technique

Annex D
(informative)

Interlaboratory trial

An interlaboratory trial was organized in the United Kingdom by the LEAP Proficiency Scheme in 1998 with laboratories from Austria, Belgium, Germany, France, Italy, the Netherlands and the United Kingdom participating. The variety of instruments and other analytical conditions used conformed with the quality parameters specified in the method.

For the description of sample matrix, see Table D.1.

The statistical results of data evaluated in accordance with ISO 5725-2 are presented in Table D.2.

The coefficients of variation of the procedure Vxo (obtained from determined calibration functions analogous to those described in 10.2) are listed in Table D.3. The data came from laboratories participating in the above-mentioned interlaboratory trial.

Table D.1 — Description of sample matrix

Sample No.	**1**	**2**	**3**	**4**	**5**
Determinand	**Concentration[a] / value**				
Conductivity (µS/cm)	< 10	567	197	347	202
Calcium (Ca^{2+})	< 2	81,7	24,4	49,7	37,3
Magnesium (Mg^{2+})	< 2	19,2	2,05	7,5	1,25
Total hardness ($CaCO_3$)	< 5	283	70	155	97,5
Alkalinity (HCO_3^-)	< 10	267	26	79	110
Chloride (Cl^-)	< 10	41	14	21	6,1
Sulfate (SO_4^{2-})	< 10	44	44	72	4,3
Total Organic Carbon (TOC)	< 0,3	0,3	2,14	2,2	0,95
Bromide (Br^-)	< 0,01	0,042	0,019	0,036	0,015
Chlorite (ClO_2^-)	< 0,01	< 0,01	< 0,01	< 0,01	< 0,01
Chlorate (ClO_3^-)	< 0,01	< 0,01	0,07	< 0,01	< 0,01
Iron (Fe)	< 0,02	< 0,02	0,043	< 0,02	< 0,02
Aluminium (Al)	< 0,01	< 0,01	0,025	0,059	< 0,01
Manganese (Mn)	< 0,005	< 0,005	< 0,005	0,012	< 0,005
Phosphorus (P)	< 0,1	< 0,1	0,82	< 0,1	< 0,1
Nitrate (NO_3^-)	< 1	7,2	2,9	15,6	< 1

[a] Concentration in milligrams per litre unless stated otherwise.

Table D.2 — Statistical data for bromate

Sample	Matrix	n	l	KA_1 %	X_{ref} µg/l	X µg/l	RR %	s_R µg/l	VC_R %	s_r µg/l	VC_r %
1	Synthetic	85	20	15,0	5,7	5,436	95,4	0,225	4,1	0,167	3,1
2	High total hardness borehole water sample	82	19	10,9	2,7	2,494	92,4	0,496	19,9	0,213	8,5
3	Low-hardness tapwater	80	19	14,0	8,6	8,265	96,1	1,411	17,1	0,498	6,0
4	Ozonylated final treated water	73	19	20,6	—	8,125	—	1,165	14,3	0,43	5,3
5	Granulate active carbon treated water	83	19	10,8	—	3,926	—	0,644	16,4	0,285	7,3

n	is the number of outlier-free individual 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;
X	is the total mean;
RR	is the recovery rate;
s_R	is the standard deviation of the reproducibility;
VC_R	is the coefficient of the reproducibility;
s_r	is the standard deviation of the repeatability;
VC_r	is the coefficient of the repeatability.

Table D.3 — Estimation of performance characteristics for bromate indicated by coefficients of variation of the procedure (Vxo) in accordance with ISO 8466-1 and ISO 8466-2

Examined working range µg/l	**Calibration mode**	**Range of** Vxo % represented by 80 % of all labs	**Range of** Vxo % represented by 20 % of all labs
1,0 to 20	ISO 8466-1	0,04 to 3,0	3,2 to 5,7
1,0 to 20	ISO 8466-2	0,03 to 2,7	3,1 to 5,6

Annex E
(informative)

Checked interferences

Table E.1 — Checked interferences

Checked bromate concentration		Checked organic compound and concentration added to bromate standard solution	Checked bromate recovery %
10 µg/l bromate	+	1 000 µg/l phthalic acid	Not determined
10 µg/l bromate	+	1 000 µg/l oxalic acid	Not determined
10 µg/l bromate	+	1 000 µg/l malonic acid	Not determined
10 µg/l bromate	+	1 000 µg/l succinic acid	Not determined
10 µg/l bromate	+	1 000 µg/l glutamic acid	Not determined
10 µg/l bromate	+	1 000 µg/l glyoxylic acid	Not determined
10 µg/l bromate	+	1 000 µg/l ketomalonic acid	Not determined
10 µg/l bromate	+	1 000 µg/l pyruvic acid	Not determined
10 µg/l bromate	+	100 µg/l monochloroacetic acid	Not determined
10 µg/l bromate	+	100 µg/l monobromoacetic acid	Not determined
5 µg/l bromate	+	10 000 µg/l phenol	95 to 105
5 µg/l bromate	+	1 000 µg/l saccharose and D-galactose, each (mixture)	95 to 105
5 µg/l bromate	+	1 000 µg/l D-glucosamin	95 to 105
5 µg/l bromate	+	1 000 µg/l glycine	95 to 105
5 µg/l bromate	+	1 000 µg/l urea	95 to 105
5 µg/l bromate	+	1 000 µg/l L-leucine and L-glutamine, each (mixture)	95 to 105
5 µg/l bromate	+	1 000 µg/l L-phenylamine	95 to 105
5 µg/l bromate	+	1 000 µg/l albumin	95 to 105
5 µg/l bromate	+	2 000 µg/l acetate, 4 000 µg/l formate, and 4 000 µg/l oxalate (mixture)	95 to 105
5 µg/l bromate	+	1 000 µg/l butyric acid, pyruvic acid and gycolic acid, each (mixture)	95 to 105
5 µg/l bromate	+	1 000 µg/l trichloroacetic acid	95 to 105
5 µg/l bromate	+	4 000 µg/l fulvic acid	92 to 93
5 µg/l bromate	+	2 000 µg/l humic acid	100

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