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Water quality — Determination of dissolved bromate — Method using ion chromatography (IC) and post column reaction (PCR)

Qualité de l'eau — Détermination du bromate dissous — Méthode utilisant la chromatographie ionique (IC) et la réaction post-colonne (PCR)

Reference number
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Foreword

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International Standards are drafted in accordance with the rules given in the ISO/IEC Directives, Part 2.

The main task of technical committees is to prepare International Standards. 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 document may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights.

ISO 11206 was prepared by Technical Committee ISO/TC 147, *Water quality*, Subcommittee SC 2, *Physical, chemical and biochemical methods*.

Water quality — Determination of dissolved bromate — Method using ion chromatography (IC) and post column reaction (PCR)

WARNING — Persons using this International Standard should be familiar with normal laboratory practice. This standard 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 ensure compliance with any national regulatory conditions.

IMPORTANT — It is absolutely essential that tests conducted according to this International Standard be carried out by suitably trained staff.

1 Scope

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

Appropriate pretreatment of the sample (e.g. dilution) allows determination of bromate at concentrations ≥0,5 µg/l.

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

2 Normative references

The following referenced documents are indispensable for the application 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 Interferences

Metals present in samples and eluents bind to the resin material of the separator column, resulting in a loss of performance. Metal ions can be eliminated with the aid of special cation exchangers (see 6.2 and Clause 8, Note 1).

Solid particles and organic compounds (e.g. mineral oils, detergents, and humic acids) shorten the lifetime of the precolumn and the separator column (see Clause 8, Notes 2 and 3).

Chlorite can interfere with the determination of bromate. Remove chlorite in accordance with the procedure specified in 9.4, if necessary.

NOTE Any substance that has a retention time coinciding with bromate and that produces a detector response can interfere. A high concentration of ions can have an impact on the resolution and on the analyte's retention time. Sample dilution and/or gradient elution overcomes much interference.

4 Principle

The sample is pretreated in order to remove ozone, chlorine dioxide, chlorite, metals and solids, if necessary (see Clause 8). Bromate is separated by ion chromatography (IC). An anion exchange resin is used as the stationary phase and either acids (e.g. sulfuric acid) or aqueous solutions of salts of weak monobasic acids

and dibasic acids are used as eluents for isocratic or gradient elution (e.g. carbonate-, hydrogen carbonate-, hydroxide-eluent, e.g. manually, automatically or in situ electrochemically prepared) (5.13).

Detection of bromate [$\rho(BrO_3^-) \geq 0{,}5$ µg/l] is achieved by applying an acidic solution of potassium iodide containing a catalytic amount of molybdenum(VI), where the bromate reacts with iodide to form the tri-iodide ion in a post column reaction (PCR) step, which is measured by its UV absorption at 352 nm.

NOTE This method can be combined with ISO 10304-1[2], ISO 10304-4[3], and ISO 15061[4].

The concentration of bromate is determined after a calibration according to ISO 8466-1 or ISO 8466-2 of the overall procedure.

Control experiments are necessary to check the validity of the calibration function (9.5). Replicate determinations can be necessary. Use of the method of standard addition may be required if matrix interferences are expected (9.3).

5 Reagents

Use only reagents of pro analysis grade. Weigh the reagents with an accuracy of ±1 % of the nominal mass, unless stated otherwise. Prepare alternative volumes of solutions as described in 5.13 to 5.19, if necessary.

5.1 Water, ISO 3696, grade 1.

5.2 Sodium carbonate, Na_2CO_3.

5.3 Sulfuric acid, $c(H_2SO_4) = 1$ mol/l.

5.4 Sodium hydroxide, NaOH.

5.5 Potassium hydroxide, KOH.

5.6 Sodium hydrogencarbonate, $NaHCO_3$.

5.7 Ammonium heptamolybdate tetrahydrate, $(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$.

5.8 Potassium iodide, KI.

5.9 Nitric acid, $\rho(HNO_3) = 1{,}41$ g/ml.

5.10 Iron(II) sulfate heptahydrate, $FeSO_4{\cdot}7H_2O$.

5.11 Potassium bromate, $KBrO_3$.

5.12 Ethylenediamine, $C_2H_8N_2$, 99 %.

5.13 Eluents.

Degas all eluents used. Take steps to avoid any renewed air pick-up during operation (e.g. by helium sparging, in-line degasser).

The choice of eluent depends 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 specified in Clause 7. Use eluents as long as the requirements in Clause 7 and in 9.3 are met.

A selection of reagents for common eluents is presented in 5.2 to 5.6. Examples for appropriate eluents are given in 5.13.2 and 5.13.3.

5.13.1 Sodium carbonate concentrate, $c(Na_2CO_3) = 0,09$ mol/l.

The addition of the following eluent concentrate is appropriate for the eluent preparation (5.13.2):

Dissolve 9,54 g of sodium carbonate (5.2) in water (5.1) in a 1 000 ml volumetric flask and dilute to volume with water (5.1).

The solution is stable for 6 months if stored at 2 °C to 8 °C.

5.13.2 Sodium carbonate eluent, $c(Na_2CO_3) = 0,009$ mol/l.

The following eluent is applicable for the determination of bromate:

Place 100 ml of the sodium carbonate concentrate (5.13.1) in a 1 000 ml volumetric flask and dilute to volume with water (5.1).

5.13.3 Sulfuric acid eluent, $c(H_2SO_4) = 0,1$ mol/l.

Place 100 ml of sulfuric acid (5.3) in a 1 000 ml volumetric flask and dilute to volume with water (5.1).

NOTE Ammonium heptamolybdate tetrahydrate (5.7) can be added to the eluent provided the composition meets the resulting concentration of the PCR reagent in the PCR unit (5.15).

5.14 Ammonium heptamolybdate solution, $c[(NH_4)_6Mo_7O_{24}] = 0,002$ mol/l.

Dissolve 0,25 g of ammonium heptamolybdate tetrahydrate (5.7) in 100 ml of water (5.1).

The solution is stable for 1 month if stored in a light impervious bottle at ambient temperature.

5.15 Post column reaction (PCR) reagent.

Degas all water used for the preparation of the PCR reagent. Take steps to avoid any renewed air pick-up during operation (e.g. by helium sparging).

Dissolve 45 g of potassium iodide (5.8) in approximately 500 ml of water (5.1), add 25 ml of the ammonium heptamolybdate solution (5.14) in a 1 000 ml volumetric flask and dilute to volume with water (5.1).

Sparge the solution with helium for 20 min to remove all traces of dissolved oxygen, and immediately place it in the PCR module and pressurize it with helium.

The solution contains 0,27 mol/l potassium iodide and 0,05 mmol/l of ammonium heptamolybdate. Prepare the solution on the day of use. Store the solution in light-impervious bottles (e.g. wrapped with aluminium foil) and protect the solution from light exposure.

NOTE Since potassium iodide is photosensitive, the solution can develop a light yellow colour with time, even when stored under helium. This can be avoided by the addition of sodium hydroxide (5.4) with a resulting concentration of 0,001 mol/l of sodium hydroxide.

5.16 Iron(II) solution, $\rho(Fe^{2+}) = 1\,000$ mg/l.

Place 6 µl of nitric acid (5.9) in approximately 15 ml water (5.1) in a 25 ml volumetric flask, dissolve 0,124 g of iron(II) sulfate heptahydrate (5.10) and dilute to volume with water (5.1).

The resulting pH value is about 2. The solution is stable for 2 d.

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

Dry approximately 1,5 g of potassium bromate (5.11) 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 (5.1) in a 1 000 ml volumetric flask and dilute to volume with water (5.1). Store the solution at 2 °C to 8 °C in polyethene or glass bottles and renew it every 12 months.

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

5.18 Bromate standard solution.

Depending on the concentrations expected, prepare the following standard solutions of different bromate concentrations from the stock standard solution (5.17). Note the possible risk of changes in concentration caused by interaction with the vessel material, which increases with decreasing bromate concentration. Store the standard solutions in polyethene or glass bottles.

5.18.1 Bromate standard solution I, $\rho(BrO_3^-) = 100$ mg/l.

Pipette 10,0 ml of bromate stock standard solution (5.17) into a 100 ml volumetric flask and dilute to volume with water (5.1).

Store the solution at 2 °C to 8 °C in polyethene or glass bottles. The solution is stable for 6 months.

5.18.2 Bromate standard solution II, $\rho(BrO_3^-) = 1$ mg/l.

Pipette 1,0 ml of standard solution I (5.18.1) into a 100 ml volumetric flask and dilute to volume with water (5.1).

Store the solution at 2 °C to 8 °C in polyethene or glass bottles. The solution is stable for 3 months.

5.19 Bromate calibration solutions.

Depending on the bromate concentration expected in the sample, use the bromate standard solution I (5.18.1) or II (5.18.2) 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 0,5 µg/l to 5 µg/l bromate.

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 and 500 µl of the bromate standard solution II (5.18.2) and dilute to volume with water (5.1).

The concentrations of bromate 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.

5.20 Blank solution.

Fill a volumetric flask, e.g. 100 ml, with water (5.1).

6 Apparatus

Usual laboratory apparatus and, in particular, the following.

6.1 IC system, complying with the quality requirements specified in Clause 7, i.e. resolution. In general, it shall consist of the following components (see Figure 1).

6.1.1 Eluent reservoir, and a degassing unit.

6.1.2 IC pump, suitable for isocratic or gradient technique.

6.1.3 Sample delivery device, e.g. sample pump, including a sample injection system incorporating a sample loop of appropriate volume (e.g. 0,1 ml to 1 ml) or autosampler device.

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

6.1.5 Post column reaction (PCR) unit, consisting of the following:

6.1.5.1 PCR reagent reservoir.

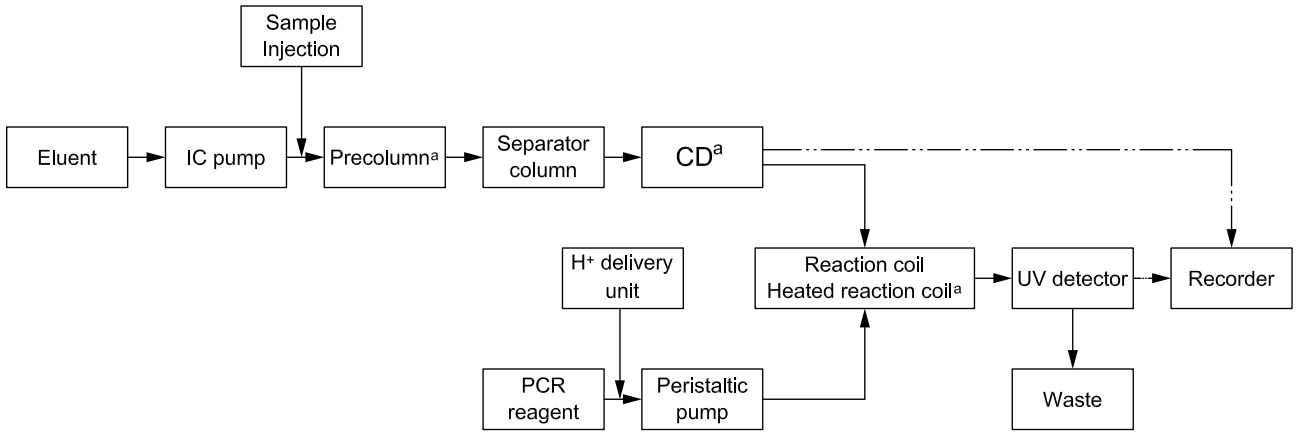
6.1.5.2 H^+ delivery unit, e.g. H_2SO_4 reservoir, suppressor unit.

6.1.5.3 Reagent delivery system, e.g. peristaltic pump.

6.1.5.4 Reaction coil, of e.g. 500 µl internal volume.

6.1.5.5 Reaction coil heater, capable of maintaining a temperature of 80 °C.

6.1.6 UV detector, e.g. spectrophotometer: 190 nm to 400 nm.



Key

CD conductivity detector

[a] Optional.

Figure 1 — Schematic representation of an ion chromatographic system including an in-line PCR system

6.2 Cartridges.

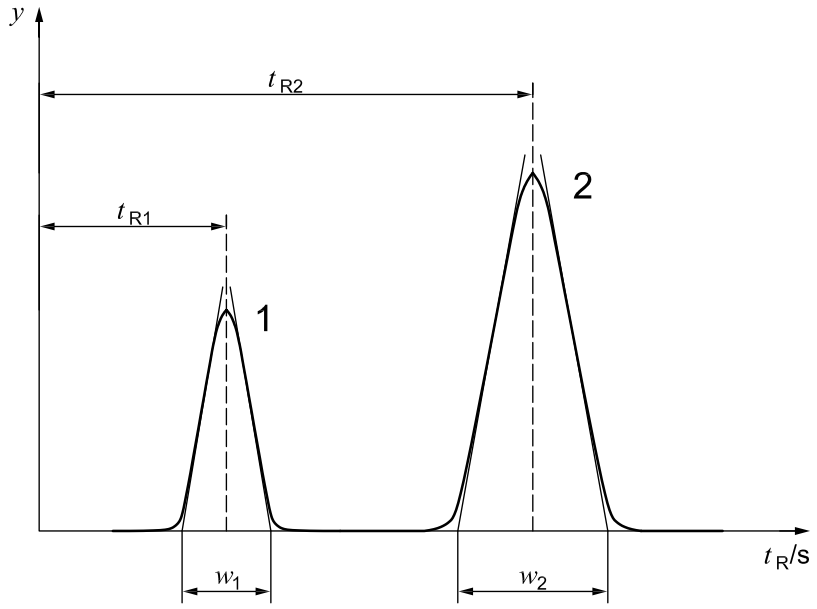
6.2.1 Cation exchanger in the Na form (cartridge).

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

7 Quality requirements

7.1 Separator column

In chromatograms of samples and standard solutions of bromate, the peak resolution, R, between bromate and the nearest peak shall not fall below 1,3 [see Equation (1) and Figure 2]. Adjust the separation conditions accordingly.



Key

w_1 width of peak 1
w_2 width of peak 2
t_R retention time
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 International Standard, the calculation of resolution, R, is appropriate for both isocratic and gradient elution.

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

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

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 The values w_1 and w_2 are the base widths of the isosceles triangles constructed over each Gaussian peak.

7.2 PCR conditions

Typical analytical conditions are described in 7.3 and 7.4.

Adjust the ammonium heptamolybdate concentration to between 11 µmol/l and 15 µmol/l and the potassium iodide concentration to between 55 mmol/l and 65 mmol/l.

Alterations of the procedural parameters (e.g. flow rates, potassium iodide concentration or ammonium heptamolybdate concentration in eluent or PCR reagent) are allowed. If applied, calculate using Equation (2):

$$q_{V1} \cdot c_1 + q_{V2} \cdot c_2 = (q_{V1} + q_{V2}) \cdot c_3 \quad (2)$$

where

q_{V1} is the eluent flow rate, in millilitre per minute;

c_1 is the concentration, in mole per litre, of ammonium heptamolybdate solution in the eluent;

q_{V2} is the flow rate, in millilitre per minute, of the PCR pump;

c_2 is the concentration, in mole per litre, of ammonium heptamolybdate or potassium iodide solution in the PCR reagent;

c_3 is the concentration, in mole per litre, of ammonium heptamolybdate or potassium iodide solution after the mixing procedure in the PCR unit.

EXAMPLE Example for the calculation of the ammonium heptamolybdate concentration in the PCR module

Eluent flow: $q_{V1} = 0{,}7$ ml/min

Ammonium heptamolybdate concentration in the eluent: $c_1 = 0$ µmol/l

PCR flow: $q_{V2} = 0{,}2$ ml/min

Ammonium heptamolybdate concentration in the PCR reagent: $c_2 = 50$ µmol/l

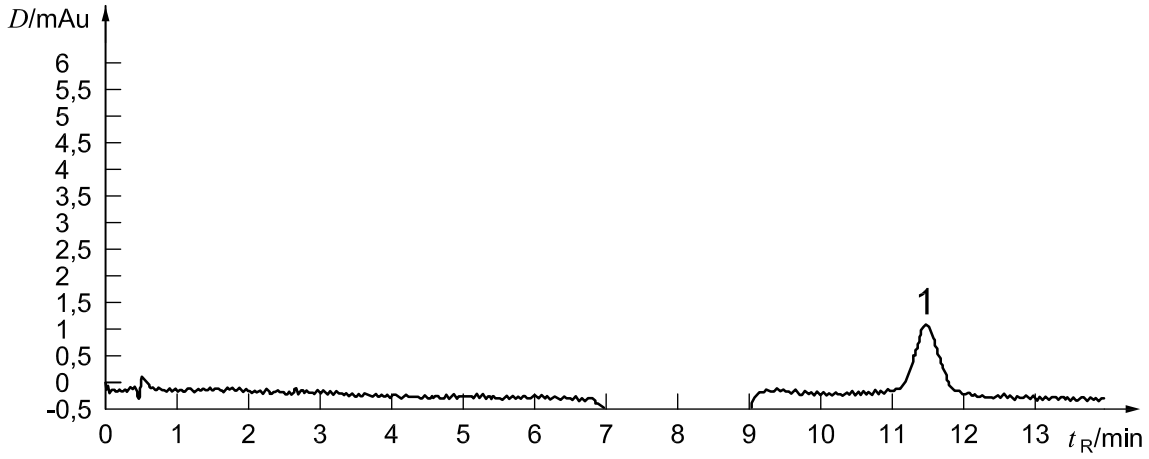
$0{,}7 \text{ ml/min} \cdot 0 \text{ µmol/l} + 0{,}2 \text{ ml/min} \cdot 50 \text{ µmol/l} = (0{,}7 \text{ ml/min} + 0{,}2 \text{ ml/min}) \cdot c_3$

Ammonium heptamolybdate concentration in the PCR module: $c_3 = 11{,}1$ µmol/l

NOTE Solutions with a pH value >1 can require heating of the reaction solution in the PCR unit.

7.3 Chromatographic and PCR conditions for the chromatogram shown in Figure 3

Column:	Ion exchanger
Eluent:	100 mmol/l sulfuric acid
Sample injection volume:	1 000 µl
Eluent flow rate:	0,7 ml/min
PCR reagent:	0,27 mol/l potassium iodide + 50 µmol/l ammonium heptamolybdate
PCR reagent flow:	0,2 ml/min
Conditions at PCR reaction coil:	Volume: 400 µl
	Temperature: ambient temperature
	11,1 µmol/l ammonium heptamolybdate
	60 mmol/l potassium iodide
Detection:	UV, $\lambda = 352$ nm



Key

D absorbance

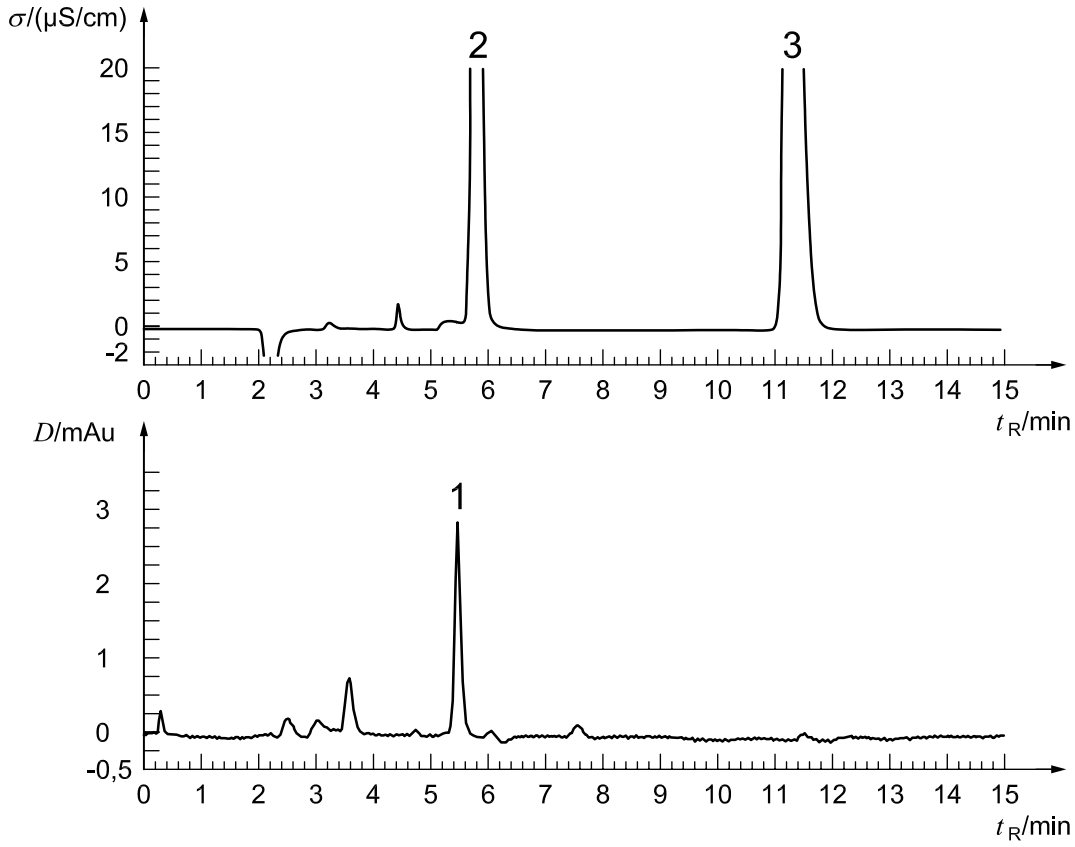
t_R retention time

Peak	Ion	Concentration
1	bromate	1,0 µg/l

Figure 3 — Example of a chromatogram of a standard solution conforming to this International Standard

7.4 Chromatographic and PCR conditions for the chromatogram shown in Figure 4

Precolumn:	Ion exchanger
Column:	Ion exchanger
Eluent:	9 mmol/l Na_2CO_3
Sample injection volume:	225 µl
Eluent flow rate:	1,3 ml/min
PCR reagent:	0,27 mol/l potassium iodide + 50 µmol/l ammonium heptamolybdate
PCR reagent flow:	0,4 ml/min
Conditions at PCR reaction coil:	Volume: 375 µl
	Temperature: 80 °C
	12 µmol/l ammonium heptamolybdate
	64 mmol/l KI
Detection:	UV, $\lambda = 352$ nm



Key

σ conductivity

D absorbance

t_R retention time

Peak	Ion	Concentration
1	bromate	8 µg/l
2	chloride	14 mg/l
3	sulfate	19 mg/l

Figure 4 — Example of chromatograms of a drinking water sample conforming to this International Standard

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

8 Sampling and sample pretreatment

Use clean polyethene vessels for sampling.

Avoid any further formation of bromate after sampling by immediately removing any ozone present by the addition of 50 mg of ethylenediamine (5.12) to 1 l of sample immediately after sampling.

NOTE 1 Metals present can be eliminated with the aid of cation exchangers (e.g. cartridge in the Na form).

NOTE 2 Solids can be removed with the aid of a membrane filter of pore size 0,45 µm.

NOTE 3 Organic compounds and solids can be removed with the aid of a non-polar adsorbant (e.g. SPE cartridge, on-line column, on-line dialysis).

Treat the calibration solutions (5.19) and the blank solution (5.20) in the same way as the sample solution.

9 Procedure

9.1 General

Set up the ion chromatographic system (6.1), including the PCR unit, in accordance with the instrument manufacturer's instructions.

Run the eluent and the PCR reagent delivery system. Once the baseline is stable, analysis can begin.

Perform the calibration as specified in 9.2. Measure the samples and blank solution (5.20) in accordance with the procedure specified in 9.3.

9.2 Calibration

Inject the pretreated bromate calibration solutions (5.19 and Clause 8). 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.

Prepare the bromate calibration solutions as described in 5.19 and Clause 8.

Analyse the calibration solutions chromatographically.

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 (9.5).

9.3 Measurement of bromate

After establishing the calibration function, inject the pretreated sample (see Clause 8) into the chromatograph and measure the peaks as described above (see Clause 9). Prior to injection into the analyser, filter the sample through a membrane filter (of pore size 0,45 µm) 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 bromate peak by comparing the retention time with that of bromate in the calibration solutions (5.19). Deviation of retention times shall not exceed ±10 % within a batch.

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, if necessary.

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 (5.20) in the same way.

NOTE Because the potassium iodide PCR solution is susceptible to oxidation, resulting in a yellowish solution, it can be flushed from all parts of the equipment (e.g. reaction coil and detector cell) with water upon completion of the final analysis and prevented from draining through the reaction coil by gravity once the system is shut down.

9.4 Chlorite removal

If the chromatogram shows interference with bromate due to chlorite, remove chlorite as follows.

Place a 10 ml aliquot of sample in a 20-ml beaker, adjust the pH to 5 to 6 by adding sulfuric acid (5.3), add 40 µl of iron(II) solution (5.16), mix and allow to react for 10 min. Filter the solution through a membrane filter (of pore size 0,45 µm) to remove precipitated ferric hydroxide. Then pass the filtrate through a conditioned cation

exchanger cartridge in the Na form (6.2.1) at a flow rate of approximately 1 ml/min to remove excess soluble iron. Discard the first 3 ml, and collect an appropriate volume for analysis. The treated sample is stable for 24 h.

Spike a second 10 ml aliquot of the sample with bromate at a level close to twice the level determined in the native sample. Treat this spiked sample aliquot in the same manner as described above. Bromate recovery shall be in the range of 80 % to 120 %.

Treat the calibration solutions (5.19) and the blank solution (5.20) in the same way as the sample solution.

9.5 Validity check of the calibration function

In order to verify the continuing validity of the calibration function, measure independent standard solutions of different bromate concentrations in the lower and upper third of the working range. Proceed accordingly after the set-up procedure (see 9.1) and after each sample series at least, but in any case after 20 measurements. Recovery shall be within 90 % to 110 % of the nominal value. Recalibrate if necessary.

10 Calculation

Calculate the mass concentration, ρ, in microgram per litre or milligram per litre, of bromate in the solution using the peak areas or peak heights as specified in ISO 8466-1 or ISO 8466-2.

Take into account all of the dilution steps.

11 Expression of results

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

EXAMPLE

Bromate (BrO_3^-) 5,1 µg/l

Bromate (BrO_3^-) 0,62 µg/l

12 Test report

The test report shall contain at least the following information:

a) the test method used, together with a reference to this International Standard (ISO 11206:2011);

b) the identity of the water sample;

c) the test results obtained, expressed in accordance with Clause 11;

d) a description of sample pretreatment if relevant;

e) any deviation from this method and report of circumstances that may have affected the results.

Annex A
(informative)
Precision data

An interlaboratory trial was organized by the Institute for Reference Materials and Measurements (IRMM) of the European Commission Directorate Joint Research Centre (JRC) in 2009 with participating laboratories from Belgium, France, Germany, India, Republic of Korea, Poland, Switzerland, United Kingdom, and USA. The variety of instruments and other analytical conditions used conformed with the quality parameters specified in the method.

The statistical data of results evaluated in accordance with ISO 5725-2[1] are presented in Table A.1.

For a description of the sample matrix see Table A.2.

The coefficients of variation, V_{x0}, of the procedure (obtained from determined calibration functions analogous to those described in 9.2) are listed in Table A.3. These data come from expert laboratories and were elaborated during the validation process of the method.

Table A.1 — Precision data

Sample	Matrix	l	n	o	X	$\bar{\bar{x}}$	η	s_R	$C_{V,R}$	s_r	$C_{V,r}$
				%	µg/l	µg/l	%	µg/l	%	µg/l	%
1	Drinking water, soft	13	52	7,1	2,61	2,68	97,4	0,132	5,1	0,084	3,2
2	Drinking water, hard	12	48	14,3	8,93	10,0	89,3	0,476	5,3	0,112	1,3
3	Mineral water	11	44	21,4	2,94	3,00	98,1	0,107	3,6	0,067	2,3
4	Swimming pool water	12	48	14,3	7,66	—	—	0,171	2,2	0,095	1,2
5	Raw water	14	55	1,8	7,86	7,95	98,9	0,243	3,1	0,125	1,6
6	Blank[a]	14	—	—	—	—	—	—	—	—	—
7	Synthetic standard	14	56	0	1,65	1,67	99,0	0,097	5,9	0,068	4,1

l	number of laboratories after outlier rejection
n	number of individual test results after outlier rejection
o	percentage of outliers
X	assigned value
$\bar{\bar{x}}$	overall mean of results (without outliers)
η	recovery rate
s_R	reproducibility standard deviation
$C_{V,R}$	coefficient of variation of reproducibility
s_r	repeatability standard deviation
$C_{V,r}$	coefficient of variation of repeatability

NOTE All data employed in the calculation in accordance with ISO 5725-2[2] are used by kind permission of IRMM.

a None of the participants reported a quantitative value for the blank sample.

Table A.2 — Description of sample matrices (analysed before spiking with bromate and ethylenediamine)

Measurand	Unit	Sample				
		1	2	3	4	5
		Disinfection agent				
		ClO_2	ClO_2	none	ClO_2	unknown
Acid capacity (pH 4,3)	mmol/l	1,1	5,1	3,7	2	3,6
Base capacity (pH 8,2)	mmol/l	≤0,02	0,06	0,12	0,04	0,08
Hardness $\Sigma(Ca^{2+}+Mg^{2+})$	mmol/l	0,7	3,4	2,0	2,7	2,7
Total bound nitrogen (TN_b)	mg/l	2,7	1,1	2,0	2,4	2,1
Total inorganic carbon (TIC)	mg/l	13	61	47	24	44
Total organic carbon (TOC)	mg/l	1	2,7	≤1	2,2	1,4
Aluminium (Al)	mg/l	0,01	0,02	≤0,01	0,16	0,02
Antimony (Sb)	mg/l	≤0,000 5	≤0,000 5	≤0,000 5	≤0,000 5	≤0,000 5
Arsenic (As)	mg/l	≤0,000 5	≤0,000 5	≤0,000 5	0,001	0,002
Barium (Ba)	mg/l	0,02	0,12	≤0,01	0,06	0,05
Boron (B)	mg/l	0,02	0,05	0,03	0,05	0,05
Cadmium (Cd)	mg/l	≤0,000 5	≤0,000 5	≤0,000 5	≤0,000 5	≤0,000 5
Calcium (Ca)	mg/l	20	110	80	88	85
Chromium (Cr)	mg/l	≤0,002	≤0,002	≤0,002	0,002	≤0,002
Copper (Cu)	mg/l	0,004	0,17	0,002	0,004	0,003
Iron (Fe)	mg/l	0,009	0,088	≤0,01	0,001	0,002
Lead (Pb)	mg/l	≤0,000 5	0,003	≤0,000 5	≤0,000 5	≤0,000 5
Magnesium (Mg)	mg/l	4,8	17	0,74	13	13
Manganese (Mn)	mg/l	0,003	0,002	≤0,000 5	≤0,000 5	≤0,000 5
Nickel (Ni)	mg/l	0,001	0,003	≤0,001	0,002	0,004
Potassium (K)	mg/l	1,0	2,6	0,2	3,6	3,1
Selenium (Se)	mg/l	≤0,005	≤0,005	≤0,005	≤0,005	≤0,005
Silicon (Si)	mg/l	8,8	7,7	2,4	3,3	3,1
Sodium (Na)	mg/l	7,4	17	1,8	77	28
Tin (Sn)	mg/l	0,000 5	0,016	≤0,000 5	≤0,000 5	≤0,000 5
Zinc (Zn)	mg/l	0,01	0,05	≤0,01	0,008	0,003
Ammonium (NH_4^+-N)	mg/l	≤0,07	≤0,07	≤0,07	≤0,07	≤0,07
Bromide (Br^-)	mg/l	0,06	0,06	≤0,05	0,03	0,1
Chloride (Cl^-)	mg/l	9,5	34	2,9	140	63
Chlorite (ClO_2^-)	mg/l	0,06	≤0,01	≤0,01	≤0,01	≤0,01
Fluoride (F^-)	mg/l	0,1	0,17	0,02	0,19	0,17
Nitrate (NO_3^--N)	mg/l	2,3	0,52	1,5	1,9	1,7
Nitrite (NO_2^--N)	mg/l	<0,02	<0,02	≤0,02	<0,02	<0,02
o-Phosphate (PO_4^{3-}-P)	mg/l	0,008	0,012	≤0,005	0,02	0,039
Total phosphorous (P)	mg/l	0,17	0,17	0,1	0,1	0,11
Sulfate (SO_4^{2-})	mg/l	19	67	18	140	48

Table A.3 — Estimation of performance characteristics as specified in ISO 8466-1 and ISO 8466-2 indicated by the coefficient of variation of the procedure, V_{x0}

Method according to	Working range	Signal used	V_{x0} (ISO 8466-1)	V_{x0} (ISO 8466-2)
	µg/l		%	%
7.3	0,5 to 5,0	Peak area	1,15	1,18
7.4	0,5 to 5,0	Peak area	1,72	1,82

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