
**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)*

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ISO 11206:2011

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Contents	Page
Foreword	iv
1 Scope	1
2 Normative references	1
3 Interferences	1
4 Principle	1
5 Reagents	2
6 Apparatus	4
7 Quality requirements	5
7.1 Separator column	5
7.2 PCR conditions	6
7.3 Chromatographic and PCR conditions for the chromatogram shown in Figure 3	7
7.4 Chromatographic and PCR conditions for the chromatogram shown in Figure 4	8
8 Sampling and sample pretreatment	9
9 Procedure	10
9.1 General	10
9.2 Calibration	10
9.3 Measurement of bromate	10
9.4 Chlorite removal	10
9.5 Validity check of the calibration function	11
10 Calculation	11
11 Expression of results	11
12 Test report	11
Annex A (informative) Precision data	12
Bibliography	15

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 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*.

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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 $\geq 0,5 \mu\text{g/l}$.

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.

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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 [$\rho(\text{BrO}_3^-) \geq 0,5 \mu\text{g/l}$] 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**, $c(\text{H}_2\text{SO}_4) = 1 \text{ mol/l}$.

5.4 **Sodium hydroxide**, NaOH .

5.5 **Potassium hydroxide**, KOH .

5.6 **Sodium hydrogencarbonate**, NaHCO_3 .

5.7 **Ammonium heptamolybdate tetrahydrate**, $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$.

5.8 **Potassium iodide**, KI .

5.9 **Nitric acid**, $\rho(\text{HNO}_3) = 1,41 \text{ g/ml}$.

5.10 **Iron(II) sulfate heptahydrate**, $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$.

5.11 **Potassium bromate**, KBrO_3 .

5.12 **Ethylenediamine**, $\text{C}_2\text{H}_8\text{N}_2$, 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, $c(\text{Na}_2\text{CO}_3) = 0,09 \text{ mol/l}$.

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, $c(\text{Na}_2\text{CO}_3) = 0,009 \text{ mol/l}$.

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, $c(\text{H}_2\text{SO}_4) = 0,1 \text{ mol/l}$.

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, $c[(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}] = 0,002 \text{ mol/l}$.

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).

Spurge 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, $\rho(\text{Fe}^{2+}) = 1 \text{ 000 mg/l}$.

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, $\rho(\text{BrO}_3^-) = 1 \text{ 000 mg/l}$.

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, $\rho(\text{BrO}_3^-) = 100 \text{ mg/l}$.

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, $\rho(\text{BrO}_3^-) = 1 \text{ mg/l}$.

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. (standards.iteh.ai)

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.

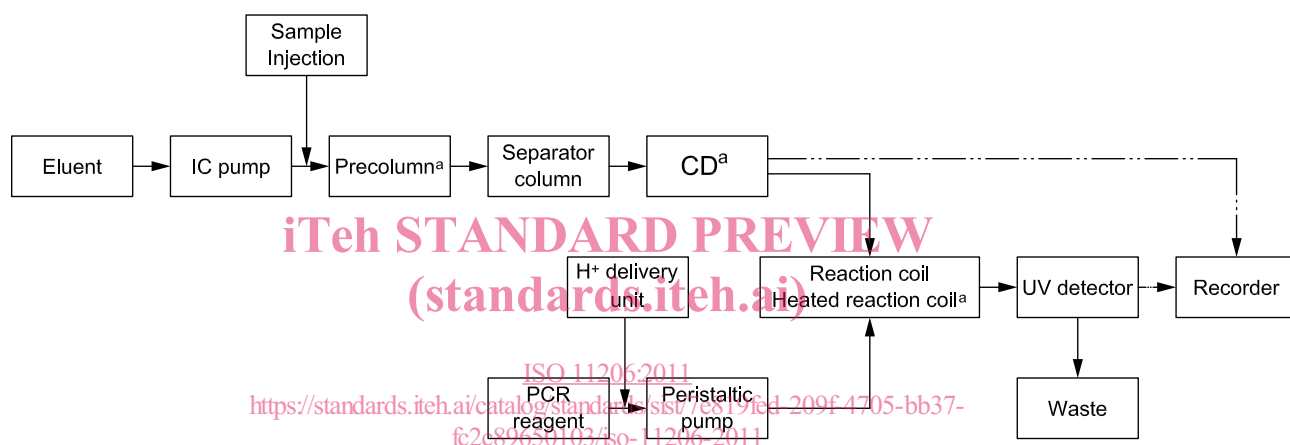
6.1.5.2 H⁺ delivery unit, e.g. H₂SO₄ reservoir, suppressor unit.

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.

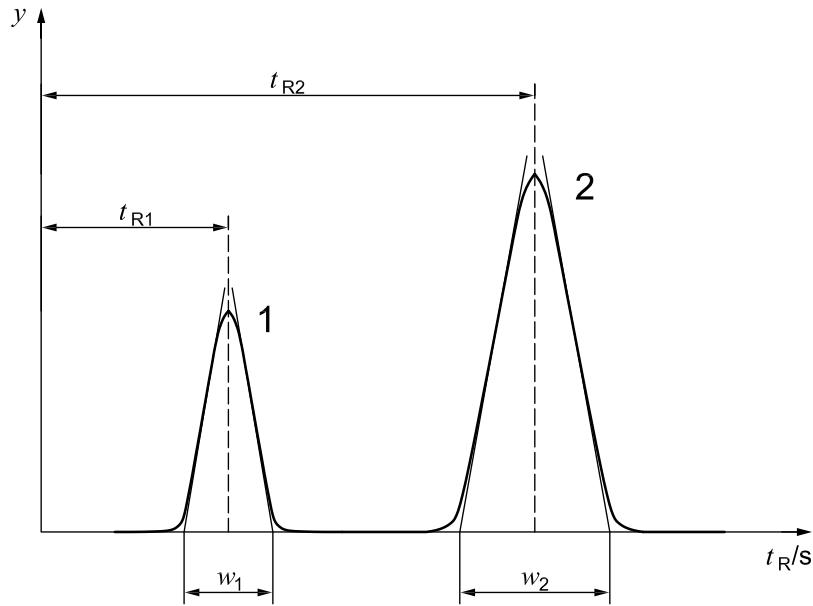
6.2.1 Cation exchanger in the Na form (cartridge).

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

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

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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):

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

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 $\mu\text{mol/l}$ and 15 $\mu\text{mol/l}$ 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: $c_1 = 0$ μ mol/l

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

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

$0,7$ ml/min \cdot 0 μ mol/l + $0,2$ ml/min \cdot 50 μ mol/l = $(0,7$ ml/min + $0,2$ ml/min) \cdot c_3

Ammonium heptamolybdate concentration in the PCR module: $c_3 = 11,1$ μ mol/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 μ l
Eluent flow rate:	0,7 ml/min
PCR reagent:	0,27 mol/l potassium iodide + 50 μ mol/l ammonium heptamolybdate
PCR reagent flow:	0,2 ml/min
Conditions at PCR reaction coil:	Volume: 400 μ l Temperature: ambient temperature 11,1 μ mol/l ammonium heptamolybdate 60 mmol/l potassium iodide
Detection:	UV, $\lambda = 352$ nm