
**Water quality — Determination
of dissolved anions by liquid
chromatography of ions —**

**Part 1:
Determination of bromide, chloride,
fluoride, nitrate, nitrite, phosphate
and sulfate**

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*Qualité de l'eau — Dosage des anions dissous par chromatographie
des ions en phase liquide —*

*Partie 1: Dosage du bromure, chlorure, fluorure, nitrate, nitrite,
phosphate et sulfate - 1-2007*



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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 10304-1 was prepared by Technical Committee ISO/TC 147, *Water quality*, Subcommittee SC 2, *Physical, chemical and biochemical methods*.

This second edition of ISO 10304-1 cancels and replaces ISO 10304-1:1992 and ISO 10304-2:1995, which have been technically revised.

ISO 10304 consists of the following parts, under the general title *Water quality — Determination of dissolved anions by liquid chromatography of ions*:

- Part 1: *Determination of bromide, chloride, fluoride, nitrate, nitrite, phosphate and sulfate*
- Part 3: *Determination of chromate, iodide, sulfite, thiocyanate and thiosulfate*
- Part 4: *Determination of chlorate, chloride and chlorite in water with low contamination*

Introduction

The user should be aware that particular problems could require the specification of additional conditions not provided for in this part of ISO 10304.

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Water quality — Determination of dissolved anions by liquid chromatography of ions —

Part 1: Determination of bromide, chloride, fluoride, nitrate, nitrite, phosphate and sulfate

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

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This part of ISO 10304 specifies a method for the determination of dissolved bromide, chloride, fluoride, nitrate, nitrite, orthophosphate and sulfate in water, e.g. drinking water, ground water, surface water, waste water, leachates and marine water by liquid chromatography of ions.

The lower limit of application is $\geq 0,05$ mg/l for bromide and for nitrite, and $\geq 0,1$ mg/l for chloride, fluoride, nitrate, orthophosphate, and sulfate. The lower limit of application depends on the matrix and the interferences encountered.

The working range may be expanded to lower concentrations (e.g. $\geq 0,01$ mg/l) if an appropriate pre-treatment of the sample (e.g. conditions for trace analyses, pre-concentration technique) is applied, and/or if an ultraviolet (UV) detector (for bromide, nitrate and nitrite) is used.

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 5667-3, *Water quality — Sampling — Part 3: Guidance on the preservation and handling of water samples*

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

3.1 Organic acids

Aliphatic organic acids such as mono- or dicarboxylic acids may interfere with the separation of the anions.

3.2 Sulfite

Sulfite may cause a positive bias for sulfate due to autooxidation. In this case the sample may be adjusted to pH 10 and formaldehyde solution is added in order to stabilize sulfite, if necessary.

3.3 Metals

The presence of metals (e.g. alkaline earth metals, transition metals, heavy metals) possibly interfering with the anions of interest, should be checked and can be eliminated with the aid of special cation exchangers (e.g. cartridge in the H-form or Na-form).

NOTE Depending on the sample matrix, the use of cation exchangers in the H-form can cause losses of fluoride and nitrite.

4 Principle

The sample is pretreated in order to remove solids (see Clause 7), sulfite and metal ions, if necessary. The anions of interest (bromide, chloride, fluoride, nitrate, nitrite, orthophosphate and sulfate), are separated by liquid chromatography, applying an anion exchange resin as stationary phase, and aqueous solutions of salts of weak mono- and dibasic acids as eluents for isocratic or gradient elution (e.g. carbonate, hydrogencarbonate, hydroxide eluent) (5.10). Detection is carried out using a conductivity detector (CD).

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When using CDs it is essential that the eluents show a sufficiently low conductivity. For this reason, CDs are usually combined with a suppressor device (cation exchanger), which will reduce the conductivity of the eluent and transform the sample species into their respective acids.

NOTE A UV detector is not required to carry out this analysis, but can be used for bromide, nitrate or nitrite if a higher sensitivity is required and/or in case of a matrix interference to the CD. If used, bromide, nitrate and nitrite can be measured at $\lambda = 200 \text{ nm}$ to $\lambda = 215 \text{ nm}$.

Check resolution, R , to ensure that it complies with the required separation conditions (6.2). UV may be used in combination with a CD. UV measures the absorption directly.

Calibration is carried out as specified in ISO 8466-1 or ISO 8466-2 (8.2). In special cases, extended working ranges (e.g. two concentration decades) may be applied.

Control experiments are necessary to check the validity of the calibration function. Replicate determinations may be necessary. Use of the method of standard addition may be required when matrix interferences are expected (8.3).

5 Reagents

Use only reagents of recognized analytical grade. Weigh the reagents with an accuracy of $\pm 1 \%$ of the nominal mass, unless stated otherwise. The reagents listed in 5.2 to 5.5 may be considered representative examples for the preparation of eluents (5.10).

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

5.2 Sodium hydrogencarbonate, NaHCO_3 .

5.3 Sodium carbonate, Na₂CO₃.

5.4 Sodium hydroxide, NaOH.

5.5 Potassium hydroxide, KOH.

5.6 Bromide, chloride, fluoride, nitrate, nitrite, orthophosphate and sulfate stock standard solutions, $\rho = 1\ 000$ mg/l each.

Single anion and mixed anion stock solutions with adequate and required specification are commercially available. These solutions are considered to be stable for several months.

For an alternative preparation of stock solutions see Table 1. Dissolve the salts accordingly, after appropriate treatment.

Table 1 — Mass portion and pre-treatment for stock solutions

Anion to be determined	Salt to be used ^a	Mass g	Pre-treatment by drying at (105 ± 5) °C for at least
Bromide	NaBr	1,287 7	6 h
Chloride	NaCl	1,648 4	2 h
Fluoride	NaF	2,210 0	1 h
Nitrate	NaNO ₃	1,370 7	24 h
Nitrite	NaNO ₂	1,499 8	1 h
Orthophosphate	KH ₂ PO ₄	1,433 0	1 h
Sulfate	Na ₂ SO ₄	1,478 6	1 h

^a Alternative salts with adequate and required specification may be used.

5.7 Bromide, chloride, fluoride, nitrate, nitrite, orthophosphate and sulfate standard solutions

5.7.1 General

Depending on the concentrations expected, prepare single or mixed standard solutions, of bromide, chloride, fluoride, nitrate, nitrite, orthophosphate and sulfate concentrations from the stock standard solution (5.6). Store the standard solutions in polyethene bottles.

5.7.2 Example for a bromide, chloride, fluoride, nitrate, nitrite, orthophosphate and sulfate mixed standard solution, $\rho = 10$ mg/l each.

Pipette 1,0 ml of each of the stock standard solutions (5.6) into a 100 ml volumetric flask, and dilute to volume with water (5.1).

The solutions are stable for 1 week, if stored in the dark at 2 °C to 8 °C in polyethene bottles.

5.8 Bromide, chloride, fluoride, nitrate, nitrite, orthophosphate and sulfate calibration solutions

Depending on the concentrations expected in the sample, use the standard solution (5.7.2) to prepare e.g. 5 to 10 calibration solutions distributed as evenly as possible over the expected working range.

For example, proceed as follows for the range 0,05 mg/l to 0,5 mg/l:

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Pipette, into a series of 20 ml volumetric flasks, the following volumes: 100 µl, 200 µl, 300 µl, 400 µl, 500 µl, 600 µl, 700 µl, 800 µl, 900 µl or 1 000 µl of the standard solution (5.7.2) and dilute to volume with water (5.1).

The concentrations of the anions in these calibration solutions are: 0,05 mg/l, 0,1 mg/l, 0,15 mg/l, 0,2 mg/l, 0,25 mg/l, 0,3 mg/l, 0,35 mg/l, 0,4 mg/l, 0,45 mg/l or 0,5 mg/l, respectively.

Prepare the calibration solutions on the day of use.

5.9 Blank

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

5.10 Eluents

5.10.1 General

Degas all water used for eluent preparation. In order to minimise the growth of bacteria or algae, prepare eluents freshly after 3 days.

The choice of eluent depends on the chosen column and detector (e.g. UV or conductivity), seek advice from the column supplier. The chosen combination of separator column and eluent shall meet the resolution requirements stated in 6.2.

The example for the eluent composition in 5.10.3 refers to the CD suppressor technique only. Nevertheless, the non-suppressed CD technique (as well as UV detection) is included in this method.

A selection of reagents for common eluents is given in 5.2 to 5.5.

NOTE Preparing the eluent from concentrates has proved to be successful.

5.10.2 Sodium carbonate/sodium hydrogencarbonate concentrate

For the eluent concentrate preparation:

Place 28,6 g of sodium carbonate (5.3) and 8,4 g of sodium hydrogencarbonate (5.2) into a 1 000 ml volumetric flask.

Dissolve in water (5.1) and dilute to volume with water.

The solution contains 0,27 mol/l of sodium carbonate and 0,1 mol/l of sodium hydrogencarbonate.

This solution is stable for several months if stored at 2 °C to 8 °C in glass or polyethene bottles.

5.10.3 Sodium carbonate/sodium hydrogencarbonate eluent

The following eluent is applicable for the determination of the anions according to this standard:

Pipette 20 ml of the concentrate (5.10.2) into a 2 000 ml volumetric flask and dilute to volume with water (5.1).

The solution contains 0,002 7 mol/l of sodium carbonate and 0,001 mol/l of sodium hydrogencarbonate.

6 Apparatus

Usual laboratory apparatus, and, in particular:

6.1 Ion chromatography system. In general, it consists of the following components (see Figure 1).

6.1.1 Eluent reservoir, and a degassing unit.

6.1.2 Metal-free HPLC pump.

6.1.3 Sample injection system, incorporating a sample loop of appropriate volume (e.g. 0,02 ml) or autosampler device.

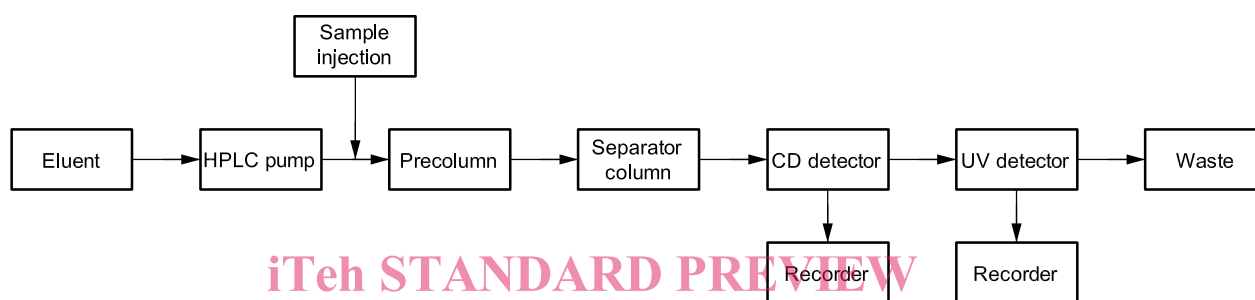
6.1.4 Separator column, with the specified separating performance (6.2).

6.1.5 Conductivity detector (CD).

6.1.6 Ultraviolet (UV) detector, e.g. a spectrophotometer, operating over the wavelength range: 190 nm to 400 nm, optionally used in combination with a CD or, as an alternative, if only bromide, nitrate or nitrite are to be determined.

6.1.7 Recording device (e.g. a computer with software for data acquisition and evaluation).

6.1.8 Precolumns, if necessary (see 3.3 and Note to 8.3).



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Figure 1 — Ion chromatographic system

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6.2 Quality requirements for the separator column

In chromatograms of samples and standard solutions (see Figure 2), the peak resolution, R , between the anion of interest and its nearest peak, shall not fall below 1,3 [see Equation (1) and Figure 3].

Separation conditions shall be such that possible interfering anions will not interfere with the anion of interest.