
**Kakovost vode - Določanje raztopljenih anionov z ionsko kromatografijo - 2. del:
Določanje bromida, klorida, nitrata, nitrita, ortofosfata in sulfata v odpadni vodi**

Water quality -- Determination of dissolved anions by liquid chromatography of ions --
Part 2: Determination of bromide, chloride, nitrate, nitrite, orthophosphate and sulfate in
waste water

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Qualité de l'eau -- Dosage des anions dissous par chromatographie des ions en phase
liquide -- Partie 2: Dosage des ions bromure, chlorure, nitrate, nitrite, orthophosphate et
sulfate dans les eaux usées

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ICS:

13.060.30	Odpadna voda	Sewage water
13.060.50	Preiskava vode na kemične snovi	Examination of water for chemical substances

SIST ISO 10304-2:1996

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INTERNATIONAL
STANDARD

ISO
10304-2

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1995-04-01

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

iTeh STANDARD PREVIEW

Part 2:

(Determination of bromide, chloride, nitrate,
nitrite, orthophosphate and sulfate in waste
water)

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

Partie 2: Dosage des ions bromure, chlorure, nitrate, nitrite, orthophosphate et sulfate dans les eaux usées



Reference number
ISO 10304-2:1995(E)

ISO 10304-2:1995(E)

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.

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.

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

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

- Part 2: *Determination of bromide, chloride, nitrate, nitrite, orthophosphate and sulfate in waste water*
- Part 3: *Determination of chromate, iodide, sulfite, thiocyanate and thiosulfate*
- Part 4: *Determination of chlorate, chloride and chlorite in water with low contamination*

The title of ISO 10304-1:1992 is *Water quality — Determination of dissolved fluoride, chloride, nitrite, orthophosphate, bromide, nitrate and sulfate ions, using liquid chromatography of ions — Part 1: Method for water with low contamination*

Annex A of this part of ISO 10304 is for information only.

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Introduction

The essential minimum requirements of an ion chromatographic system to be applied within the scope of this part of ISO 10304 are the following:

Resolution power

It is essential that the peak resolution R does not fall below 1,3 for the anion to be determined and the nearest peak (see clause 6 and figure 3).

Method of detection

a) Measurement of the electrical conductivity with or without a suppressor device, respectively.

b) Photometric measurement (UV/VIS), directly or indirectly.

Applicability of the method

Working ranges are according to table 1.

Calibration

Calibration and determination of the linear working range. Use of the method of standard addition for special cases of application (see clause 9).

Quality control of the analytical method

Validity check of the calibration function (see 8.3). Replicate determinations if necessary.

The diversity of the appropriate and suitable assemblies and the procedural steps depending on them (e.g. composition of the mobile phases) permit a global description only.

For further information on the analytical technique, refer to ISO 10304-1.

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

Part 2:

Determination of bromide, chloride, nitrate, nitrite, orthophosphate and sulfate in waste water

1 Scope

1.2 Interferences

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1.1 General

This part of ISO 10304 specifies a method for the determination of the dissolved anions bromide, chloride, nitrate, nitrite, orthophosphate and sulfate in waste waters.

The working ranges listed in table 1 may be obtained by an appropriate sample pretreatment (e.g. dilution) and by applying a conductivity detector (CD) or a UV-detector.

Table 1 — Working ranges of the analytical method

Anion	Working range mg/l	Detection direct UV-detection
Bromide (Br ⁻)	0,05 to 20	CD or UV (200 nm to 215 nm)
Chloride (Cl ⁻)	0,1 to 50	CD
Nitrate (NO ₃ ⁻)	0,1 to 50	CD or UV (200 nm to 215 nm)
Nitrite (NO ₂ ⁻)	0,05 to 20	CD or UV (200 nm to 215 nm)
Orthophosphate (PO ₄ ³⁻)	0,1 to 20	CD
Sulfate (SO ₄ ²⁻)	0,1 to 100	CD

NOTE — The working range is limited by the exchange capacity of the columns.

1.2.1 Organic acids, such as monocarboxylic or dicarboxylic acids, can interfere with the determination of inorganic anions.

1.2.2 In a buffered eluent (e.g. carbonate/hydrogen carbonate), the determination will not be influenced by the sample pH in the range of pH 2 to pH 9.

1.2.3 Large concentration differences between the anions Br⁻, Cl⁻, NO₃⁻, NO₂⁻, PO₄³⁻ and SO₄²⁻ may lead to typical cross-sensitivity interferences caused by an insufficient separation. The respective concentrations given in table 2 were typical for conductivity detectors and UV-detectors; no interferences could be observed with a sample volume of 50 µl. The data given are valid only when the quality requirements specified for the columns are met (see clause 6). The determination of chloride may be subject to interference from high fluoride concentrations.

Table 2 — Cross-sensitivity of anions

[Detection: conductivity (CD) and direct UV]

Ratio of the mass concentrations solute/interfering ion		Maximum tolerable absolute concentration of interfering ions ¹⁾ mg/l	
Br ⁻ /Cl ⁻	1:500	Cl ⁻	500
Br ⁻ /PO ₄ ³⁻	1:100	PO ₄ ³⁻	100
Br ⁻ /NO ₃ ⁻	1:50	NO ₃ ⁻	100
Br ⁻ /SO ₄ ²⁻	1:500	SO ₄ ²⁻	500
Br ⁻ /SO ₃ ²⁻	1:50 ²⁾		
Cl ⁻ /NO ₂ ⁻	1:50	NO ₂ ⁻	5
Cl ⁻ /NO ₃ ⁻	1:500	NO ₃ ⁻	500
Cl ⁻ /SO ₄ ²⁻	1:500	SO ₄ ²⁻	500
NO ₃ ⁻ /Br ⁻	1:100	Br ⁻	100
NO ₃ ⁻ /Cl ⁻	1:500 (CD) 1:2 000 (UV)	Cl ⁻	500
NO ₃ ⁻ /SO ₄ ²⁻	1:500 (CD) 1:1 000 (UV)	SO ₄ ²⁻ SO ₄ ²⁻	500 500
NO ₃ ⁻ /SO ₃ ²⁻	1:50 ²⁾		
NO ₂ ⁻ /Cl ⁻	1:250 (CD) 1:10 000 (UV)	Cl ⁻ (CD) Cl ⁻ (UV)	100 500
NO ₂ ⁻ /PO ₄ ³⁻	1:50	PO ₄ ³⁻	20
NO ₂ ⁻ /NO ₃ ⁻	1:500	NO ₃ ⁻	500
NO ₂ ⁻ /SO ₄ ²⁻	1:500 (CD) 1:1 000 (UV)	SO ₄ ²⁻ SO ₄ ²⁻	500 500
PO ₄ ³⁻ /Br ⁻	1:100	Br ⁻	100
PO ₄ ³⁻ /Cl ⁻	1:500	Cl ⁻	500
PO ₄ ³⁻ /NO ₃ ⁻	1:500	NO ₃ ⁻	400
PO ₄ ³⁻ /NO ₂ ⁻	1:100	NO ₂ ⁻	100
PO ₄ ³⁻ /SO ₄ ²⁻	1:500	SO ₄ ²⁻	500
PO ₄ ³⁻ /SO ₃ ²⁻	1:50 ²⁾		
SO ₄ ²⁻ /Cl ⁻	1:500	Cl ⁻	500
SO ₄ ²⁻ /NO ₃ ⁻	1:500	NO ₃ ⁻	400
SO ₄ ²⁻ /SO ₃ ²⁻	1:50 ²⁾		
SO ₄ ²⁻ /S ₂ O ₃ ²⁻	1:500		
SO ₄ ²⁻ /I ⁻	1:500		

1) Dilute the sample if the interfering concentration is exceeded.

2) When it is present, SO₃²⁻ will always interfere.

1.2.4 The determination of sulfate may be subject to interference by high iodide or thiosulfate concentrations.

Relations: SO₄²⁻/I⁻ or SO₄²⁻/S₂O₃²⁻ or I⁻/S₂O₃²⁻ = 1: > 500

Cross-sensitivities to other anions, such as Br⁻, Cl⁻, NO₃⁻, NO₂⁻, PO₄³⁻ and SO₄²⁻, may occur, especially in the presence of sulfite ions whose retention strongly depends on the selectivity of the separating column used. Inorganic anions such as fluoroborate or chlorite can interfere with the determination of the named inorganic anions.

NOTE 1 The identification of some anions (e.g. nitrite) or the detection of interferences (e.g. fatty acids) can be facilitated by using a conductivity detector and UV-detector placed in series.

Anion combinations (e.g. Cl⁻/I⁻) which are not listed in table 2 will not interfere in the specified range of application.

Solid particles and organic compounds (such as mineral oils, detergents and humic acids) shorten the lifetime of the separating column and are therefore eliminated before the analysis is started (see clause 7).

Sulfide ions can cause errors during the determination of sulfate; they are eliminated according to clause 7.

2 Normative references

The following standards contain provisions which, through reference in this text, constitute provisions of this part of ISO 10304. At the time of publication, the editions indicated were valid. All standards are subject to revision, and parties to agreements based on this part of ISO 10304 are encouraged to investigate the possibility of applying the most recent editions of the standards indicated below. Members of IEC and ISO maintain registers of currently valid International Standards.

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 10304-1:1992, *Water quality — Determination of dissolved fluoride, chloride, nitrite, orthophosphate, bromide, nitrate and sulfate ions, using liquid chromatography of ions — Part 1: Method for water with low contamination.*

3 Principle

Liquid chromatographic separation of ions by means of a separating column. Use of an anion exchanger as the stationary phase, and usually, aqueous solutions of salts of weak monobasic and dibasic acids as mobile phases (eluent, see 4.17). Conductivity and UV-detectors are used within this part of ISO 10304. When using conductivity detectors, it is essential that the eluents have a sufficiently low conductivity. For this reason, conductivity detectors are often combined with a suppressor device (e.g. a cation exchanger) which decreases the conductivity of the eluent and converts the separated anions into their corresponding acids.

UV-detection either measures the absorption directly (see table 1) or, in the case of anions which are transparent in the UV-range, measures the decrease in the background absorption caused by a UV-absorbing eluent (indirect measurement). If indirect UV-detection is used, the measuring wavelength depends on the composition of the eluent.

The concentration of the respective anions is determined by a calibration of the overall procedure. Particular cases may require calibration by means of standard addition (spiking).

If no suppressor device is used, it is essential that the conductivity of the eluent be as low as possible.

NOTE 2 References covering this analytical technique are summarized in annex A of ISO 10304-1:1992.

4 Reagents

Use only reagents of recognized analytical grade. Weigh with an accuracy of 1 % of the nominal mass. The water shall have an electrical conductivity of < 0,01 mS/m and shall be free of particulate matter with diameter > 0,45 µm. The increase of the electrical conductivity due to an uptake of carbon dioxide does not interfere with the determination.

4.1 Sodium hydrogencarbonate (NaHCO₃).

4.2 Sodium carbonate (Na₂CO₃).

4.3 Potassium hydrogenphthalate (C₈H₅O₄K).

4.4 Sodium tetraborate (Na₂B₄O₇·10H₂O).

4.5 Gluconic acid, w(C₆H₁₂O₇) = 50 % (V/V), aqueous solution.

4.6 Methanol (CH₃OH).

4.7 Lithium hydroxide (LiOH).

4.8 Glycerol (C₃H₈O₃).

4.9 Acetonitrile (CH₃CN).

4.10 Potassium hydroxide (KOH).

4.11 Sodium bromide (NaBr).

4.12 Sodium chloride (NaCl).

4.13 Sodium nitrate (NaNO₃).

4.14 Sodium nitrite (NaNO₂).

4.15 Potassium dihydrogenphosphate (KH₂PO₄).

4.16 Sodium sulfate (Na₂SO₄).

4.17 Eluents

Different eluents are used, their choice depending on the type of separating column and detector. Therefore, follow the column manufacturer's instructions for the exact composition of the eluent. The eluent compositions described in 4.17.1 and the last two paragraphs of 4.17.2.2 are examples only. A choice of reagents commonly used as eluents is given in 4.1 to 4.10.

Degas all the eluents or prepare eluents using degassed water. Take steps to avoid any renewed gas pick-up during operation (e.g. by helium sparging). In order to avoid the growth of bacteria or algae, store the eluents in the dark and renew every 2 d to 3 d.

4.17.1 Examples of eluents for ion chromatography using the suppressor technique

For the application of the suppressor technique, sodium hydroxide and salt solutions of weakly dissociated acids, such as sodium carbonate/sodium

hydrogencarbonate, sodium hydrogencarbonate and sodium tetraborate can be used.

4.17.1.1 Sodium carbonate/sodium hydrogencarbonate concentrate

The addition of the following eluent concentrate to the sample has proved to be successful for sample pretreatment and eluent preparation (see 4.17.1.2).

Place 25,4 g of sodium carbonate (4.2) and 25,5 g of sodium hydrogencarbonate (4.1), in a volumetric flask of nominal capacity 1 000 ml, dissolve in water (see first paragraph of this clause) and dilute to volume.

The solution contains 0,24 mol/l of sodium carbonate and 0,3 mol/l of sodium hydrogencarbonate and is stable for several months if stored at 4 °C to 6 °C.

4.17.1.2 Sodium carbonate/sodium hydrogencarbonate eluent

The following eluent is applicable for the determination of bromide, chloride, nitrite, orthophosphate, and sulfate in a single determination.

Place 50 ml of the concentrate (4.17.1.1) in a volumetric flask of nominal capacity 5 000 ml, and dilute to volume with water (see first paragraph of this clause).

The solution contains 0,002 4 mol/l of sodium carbonate and 0,003 mol/l of sodium hydrogencarbonate.

4.17.2 Examples of eluents for ion chromatography without using the suppressor technique

For ion chromatography techniques which do not utilize suppressor devices, salt solutions (e.g. potassium hydrogenphthalate, *p*-hydroxybenzoic acid, sodium borate/sodium gluconate and sodium benzoate) are used. The solutions may contain various additions, e.g. alcohols. The concentration of the salts is usually in the range of 0,000 5 mol/l to 0,01 mol/l. Concentrate and eluent solutions are prepared as described in 4.17.2.1.1 and 4.17.2.1.2. Note that some alkaline concentrate solutions of the cited salts are not stable. Adjust the pH of the eluent after the dilution of the concentrate.

4.17.2.1 Mobile phases for anion exchanger on a silica gel base

For ion chromatography using anion exchanger columns on a silica gel base, use only eluents in the pH range of 1,5 to 6,5.

4.17.2.1.1 Potassium hydrogenphthalate concentrate

The addition of the following eluent concentrate to the sample has proved to be helpful for sample pretreatment and eluent preparation (4.17.2.1.2).

Place 20,5 g of potassium hydrogenphthalate (4.3) in a volumetric flask of nominal capacity 1 000 ml, dissolve in water and dilute to volume.

The solution contains 0,1 mol/l of potassium hydrogenphthalate and is stable for a longer period of time if stored at 4 °C to 6 °C.

4.17.2.1.2 Potassium hydrogenphthalate eluent

For the determination of chloride, nitrate, nitrite, orthophosphate and sulfate in a single determination, the following eluent has proved to be successful.

Place 100 ml of the concentrate (4.17.2.1.1) in a volumetric flask of nominal capacity 5 000 ml. Add 500 ml of methanol (4.6), dilute with water (see first paragraph of this clause), adjust to pH 5 with potassium hydroxide (4.10) and dilute to volume.

The solution contains 0,002 mol/l of potassium hydrogenphthalate and 10 % (V/V) of methanol.

4.17.2.2 Eluents for an anion exchanger on a polymer base

Acidic as well as basic eluents may be used for ion chromatography with an anion exchanger on a polymer base.

Examples of typical acidic eluents are solutions containing potassium hydrogenphthalate. Examples of typical basic eluents are solutions containing *p*-hydroxybenzoate or sodium borate/sodium gluconate.

For the determination of chloride, nitrate, orthophosphate and sulfate in a single determination, the sodium borate/sodium gluconate eluent has proved to be successful. It is prepared in the following way.

Place 0,85 g of sodium tetraborate (4.4), and 0,22 g of lithium hydroxide (4.7) in a volumetric flask of nominal capacity 5 000 ml. Add 0,6 ml of gluconic acid (4.5), 3,1 ml of glycerol (4.8), and 600 ml of acetonitrile (4.9). Dilute to volume with water.

4.18 Stock solutions

Prepare stock solutions with mass concentration ρ of 1 000 mg/l for each of the anions: bromide, chloride, nitrate, nitrite, orthophosphate and sulfate.

Dissolve the appropriate mass of each of the substances, prepared as stated in table 3, in a small quantity of water in volumetric flasks of nominal capacity 1 000 ml. Dilute to volume with water. The solutions are stable for several months if stored at 4 °C to 6 °C.

Alternatively, use commercially available solutions of the required concentration.

NOTE 3 Nitrite is easily oxidized to nitrate and therefore nitrite standard solutions should be prepared on the day of use.

Table 3 — Mass of portion and pretreatment for stock solutions

Anion	Salt	Mass of portion g	Pretreatment by drying ¹⁾	
			Duration h	Temperature °C
Bromide	NaBr	1,287 7	6	105
Chloride	NaCl	1,648 4	2	105
Nitrate	NaNO ₃	1,370 7	24	105
Nitrite	NaNO ₂	1,499 8	1	105
Ortho-phosphate	KH ₂ PO ₄	1,433 0	1	105
Sulfate	Na ₂ SO ₄	1,479 0	1	105

1) Let the substance cool in a desiccator after drying.

4.19 Mixed standard solutions

4.19.1 Mixed standard solution I

The mass concentrations of this solution are as follows:

$$\rho(\text{Br}^-, \text{NO}_2^-, \text{PO}_4^{3-}) = 10 \text{ mg/l}$$

$$\rho(\text{Cl}^-, \text{NO}_3^-, \text{SO}_4^{2-}) = 100 \text{ mg/l}$$

Pipette the volumes given in table 4 into a volumetric flask of nominal capacity 100 ml, and dilute to volume with water.

Store these solutions in polyethylene bottles. If stored at 4 °C to 6 °C, the solutions are stable for one week.

Table 4 — Volumes of stock solutions for the preparation of the mixed standard solution I

Anion	Stock solution	Anion concentration mg/l
	ml	
Br ⁻	1	10
Cl ⁻	10	100
NO ₃ ⁻	10	100
NO ₂ ⁻	1	10
PO ₄ ³⁻	1	10
SO ₄ ²⁻	10	100

4.19.2 Mixed standard solution II

The mass concentrations of this solution are as follows:

$$\rho(\text{Br}^-, \text{NO}_2^-, \text{PO}_4^{3-}) = 1 \text{ mg/l}$$

$$\rho(\text{Cl}^-, \text{NO}_3^-, \text{SO}_4^{2-}) = 10 \text{ mg/l}$$

Pipette 10 ml of the mixed standard solution I (4.19.1) into a volumetric flask of nominal capacity 100 ml, and dilute to volume with water.

Store these solutions in polyethylene bottles.

The solution is stable for 2 d only, even if stored at 4 °C to 6 °C.

4.19.3 Mixed standard solution III

The mass concentrations of this solution are as follows:

$$\rho(\text{Br}^-, \text{NO}_2^-, \text{PO}_4^{3-}) = 0,1 \text{ mg/l}$$

$$\rho(\text{Cl}^-, \text{NO}_3^-, \text{SO}_4^{2-}) = 1,0 \text{ mg/l}$$

Pipette 1 ml of the mixed standard solution I (4.19.1) into a volumetric flask of nominal capacity 100 ml, and dilute to volume with water.

If possible, store these solutions in polytetrafluoroethylene-hexafluoropropylene (FEP) bottles or high density polyethylene (PE-HD) bottles.

The solution is not stable. Prepare it on the day of use.

4.20 Anion calibration solutions

Depending on the anion concentration expected, use the stock solutions (4.18) or the mixed standard solutions I, II and III (4.19.1 to 4.19.3), to prepare five to