

# INTERNATIONAL STANDARD

**ISO**  
**10304-2**

First edition  
1995-04-01

---

---

## **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

*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)

## 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.

© ISO 1995

All rights reserved. Unless otherwise specified, no part of this publication may be reproduced or utilized in any form or by any means, electronic or mechanical, including photocopying and microfilm, without permission in writing from the publisher.

International Organization for Standardization

Case Postale 56 • CH-1211 Genève 20 • Switzerland

Printed in Switzerland

## 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.

This document is a preview generated by EVS

This page intentionally left blank

# 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

#### 1.1 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 ( $\text{Br}^-$ )	0,05 to 20	CD or UV (200 nm to 215 nm)
Chloride ( $\text{Cl}^-$ )	0,1 to 50	CD
Nitrate ( $\text{NO}_3^-$ )	0,1 to 50	CD or UV (200 nm to 215 nm)
Nitrite ( $\text{NO}_2^-$ )	0,05 to 20	CD or UV (200 nm to 215 nm)
Orthophosphate ( $\text{PO}_4^{3-}$ )	0,1 to 20	CD
Sulfate ( $\text{SO}_4^{2-}$ )	0,1 to 100	CD
NOTE — The working range is limited by the exchange capacity of the columns.		

### 1.2 Interferences

**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  $\text{Br}^-$ ,  $\text{Cl}^-$ ,  $\text{NO}_3^-$ ,  $\text{NO}_2^-$ ,  $\text{PO}_4^{3-}$  and  $\text{SO}_4^{2-}$  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  $\mu\text{l}$ . 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 <sup>1)</sup> mg/l	
Br <sup>-</sup> /Cl <sup>-</sup>	1:500	Cl <sup>-</sup>	500
Br <sup>-</sup> /PO <sub>4</sub> <sup>3-</sup>	1:100	PO <sub>4</sub> <sup>3-</sup>	100
Br <sup>-</sup> /NO <sub>3</sub> <sup>-</sup>	1:50	NO <sub>3</sub> <sup>-</sup>	100
Br <sup>-</sup> /SO <sub>4</sub> <sup>2-</sup>	1:500	SO <sub>4</sub> <sup>2-</sup>	500
Br <sup>-</sup> /SO <sub>3</sub> <sup>2-</sup>	1:50 <sup>2)</sup>		
Cl <sup>-</sup> /NO <sub>2</sub> <sup>-</sup>	1:50	NO <sub>2</sub> <sup>-</sup>	5
Cl <sup>-</sup> /NO <sub>3</sub> <sup>-</sup>	1:500	NO <sub>3</sub> <sup>-</sup>	500
Cl <sup>-</sup> /SO <sub>4</sub> <sup>2-</sup>	1:500	SO <sub>4</sub> <sup>2-</sup>	500
NO <sub>3</sub> <sup>-</sup> /Br <sup>-</sup>	1:100	Br <sup>-</sup>	100
NO <sub>3</sub> <sup>-</sup> /Cl <sup>-</sup>	1:500 (CD)	Cl <sup>-</sup>	500
	1:2 000 (UV)	Cl <sup>-</sup>	500
NO <sub>3</sub> <sup>-</sup> /SO <sub>4</sub> <sup>2-</sup>	1:500 (CD)	SO <sub>4</sub> <sup>2-</sup>	500
	1:1 000 (UV)	SO <sub>4</sub> <sup>2-</sup>	500
NO <sub>3</sub> <sup>-</sup> /SO <sub>3</sub> <sup>2-</sup>	1:50 <sup>2)</sup>		
NO <sub>2</sub> <sup>-</sup> /Cl <sup>-</sup>	1:250 (CD)	Cl <sup>-</sup> (CD)	100
	1:10 000 (UV)	Cl <sup>-</sup> (UV)	500
NO <sub>2</sub> <sup>-</sup> /PO <sub>4</sub> <sup>3-</sup>	1:50	PO <sub>4</sub> <sup>3-</sup>	20
NO <sub>2</sub> <sup>-</sup> /NO <sub>3</sub> <sup>-</sup>	1:500	NO <sub>3</sub> <sup>-</sup>	500
NO <sub>2</sub> <sup>-</sup> /SO <sub>4</sub> <sup>2-</sup>	1:500 (CD)	SO <sub>4</sub> <sup>2-</sup>	500
	1:1 000 (UV)	SO <sub>4</sub> <sup>2-</sup>	500
PO <sub>4</sub> <sup>3-</sup> /Br <sup>-</sup>	1:100	Br <sup>-</sup>	100
PO <sub>4</sub> <sup>3-</sup> /Cl <sup>-</sup>	1:500	Cl <sup>-</sup>	500
PO <sub>4</sub> <sup>3-</sup> /NO <sub>3</sub> <sup>-</sup>	1:500	NO <sub>3</sub> <sup>-</sup>	400
PO <sub>4</sub> <sup>3-</sup> /NO <sub>2</sub> <sup>-</sup>	1:100	NO <sub>2</sub> <sup>-</sup>	100
PO <sub>4</sub> <sup>3-</sup> /SO <sub>4</sub> <sup>2-</sup>	1:500	SO <sub>4</sub> <sup>2-</sup>	500
PO <sub>4</sub> <sup>3-</sup> /SO <sub>3</sub> <sup>2-</sup>	1:50 <sup>2)</sup>		
SO <sub>4</sub> <sup>2-</sup> /Cl <sup>-</sup>	1:500	Cl <sup>-</sup>	500
SO <sub>4</sub> <sup>2-</sup> /NO <sub>3</sub> <sup>-</sup>	1:500	NO <sub>3</sub> <sup>-</sup>	400
SO <sub>4</sub> <sup>2-</sup> /SO <sub>3</sub> <sup>2-</sup>	1:50 <sup>2)</sup>		
SO <sub>4</sub> <sup>2-</sup> /S <sub>2</sub> O <sub>3</sub> <sup>2-</sup>	1:500		
SO <sub>4</sub> <sup>2-</sup> /I <sup>-</sup>	1:500		
1) Dilute the sample if the interfering concentration is exceeded.			
2) When it is present, SO <sub>3</sub> <sup>2-</sup> will always interfere.			

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

Relations:  $\text{SO}_4^{2-}/\text{I}^-$  or  $\text{SO}_4^{2-}/\text{S}_2\text{O}_3^{2-}$  or  $\text{I}^-/\text{S}_2\text{O}_3^{2-} = 1: > 500$

Cross-sensitivities to other anions, such as Br<sup>-</sup>, Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, NO<sub>2</sub><sup>-</sup>, PO<sub>4</sub><sup>3-</sup> and SO<sub>4</sub><sup>2-</sup>, 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<sup>-</sup>/I<sup>-</sup>) 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 (NaHCO<sub>3</sub>).

#### 4.2 Sodium carbonate (Na<sub>2</sub>CO<sub>3</sub>).

#### 4.3 Potassium hydrogenphthalate (C<sub>8</sub>H<sub>5</sub>O<sub>4</sub>K).

#### 4.4 Sodium tetraborate (Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub>·10H<sub>2</sub>O).

#### 4.5 Gluconic acid, $w(\text{C}_6\text{H}_{12}\text{O}_7) = 50 \text{ \% (V/V)}$ , aqueous solution.

#### 4.6 Methanol (CH<sub>3</sub>OH).

#### 4.7 Lithium hydroxide (LiOH).

#### 4.8 Glycerol (C<sub>3</sub>H<sub>8</sub>O<sub>3</sub>).

#### 4.9 Acetonitrile (CH<sub>3</sub>CN).

#### 4.10 Potassium hydroxide (KOH).

#### 4.11 Sodium bromide (NaBr).

#### 4.12 Sodium chloride (NaCl).

#### 4.13 Sodium nitrate (NaNO<sub>3</sub>).

#### 4.14 Sodium nitrite (NaNO<sub>2</sub>).

#### 4.15 Potassium dihydrogenphosphate (KH<sub>2</sub>PO<sub>4</sub>).

#### 4.16 Sodium sulfate (Na<sub>2</sub>SO<sub>4</sub>).

#### 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