

# INTERNATIONAL STANDARD

**ISO**  
**10304-1**

First edition  
1992-11-15

---

---

**Water quality — Determination of dissolved  
fluoride, chloride, nitrite, orthophosphate,  
bromide, nitrate and sulfate ions, using liquid  
chromatography of ions**

iTeh STANDARD PREVIEW

(standards.iteh.ai)

**Part 1:**  
Method for water with low contamination

ISO 10304-1:1992

[https://standards.iteh.ai/catalog/standards/sist/c9277918-24f7-4c62-a1e2-](https://standards.iteh.ai/catalog/standards/sist/c9277918-24f7-4c62-a1e2-4223175a10304-1-1992)

*Qualité de l'eau — Dosage des ions fluorure, chlorure, nitrite,  
orthophosphate, bromure, nitrate et sulfate dissous, par  
chromatographie des ions en phase liquide —*

*Partie 1: Méthode applicable pour les eaux faiblement contaminées*



Reference number  
ISO 10304-1:1992(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 10304-1 was prepared by Technical Committee ISO/TC 147, *Water quality*, Sub-Committee SC 2, *Physical, chemical, biochemical methods*.

<https://standards.iteh.ai/catalog/standards/sist/c9277918-24f7-4c62-a1e2-9ed72a910304-1-1992>

ISO 10304 consists of the following parts, under the general title *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*
- *Part 2: Method for waste water*
- *Part 3: Determination of chromate, thiocyanate and thiosulfate*

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

© ISO 1992

All rights reserved. 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

Many different ion-exchange chromatography systems can be considered. It is therefore not appropriate to indicate the type of column, mobile phase, detector type etc. that is to be used. Thus detailed information is not given at any stage during the method, although guidance is provided. However, the quality parameters which should be met by the chromatography conditions chosen are defined.

## iTeh STANDARD PREVIEW (standards.iteh.ai)

[ISO 10304-1:1992](https://standards.iteh.ai/catalog/standards/sist/c9277918-24f7-4c62-a1e2-9eef742a31b/iso-10304-1-1992)

<https://standards.iteh.ai/catalog/standards/sist/c9277918-24f7-4c62-a1e2-9eef742a31b/iso-10304-1-1992>

**iTeh STANDARD PREVIEW**  
**(standards.iteh.ai)**

This page intentionally left blank

ISO 10304-1:1992

<https://standards.iteh.ai/catalog/standards/sist/c9277918-24f7-4c62-a1e2-9eef742af31b/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

#### 1 Scope

##### 1.1 General

This part of ISO 10304 specifies a method for the determination of fluoride, chloride, nitrite, orthophosphate, bromide, nitrate and sulfate in water with low contamination (e.g. drinking water, rain water, ground water and surface water) in the following ranges:

Fluoride (F):	0,01 mg/l to 10 mg/l
Chloride (Cl):	0,1 mg/l to 50 mg/l
Nitrite (NO <sub>2</sub> ):	0,05 mg/l to 20 mg/l
Orthophosphate (PO <sub>4</sub> ):	0,1 mg/l to 20 mg/l
Bromide (Br):	0,05 mg/l to 20 mg/l
Nitrate (NO <sub>3</sub> ):	0,1 mg/l to 50 mg/l
Sulfate (SO <sub>4</sub> ):	0,1 mg/l to 100 mg/l

NOTE 1 Anion symbols are used without charges throughout the text.

In certain cases, the range of application may be changed by variations in the working conditions (e.g. sample volume, dilution, separating columns, pre-concentration techniques, sensitivity ranges of detectors, etc.).

##### 1.2 Interferences

**1.2.1** Some organic acids, such as malonic acid, maleic acid and malic acid, may interfere in the determination of inorganic anions if they are present in high concentrations.

**1.2.2** The determination of fluoride in particular is subject to interference by formic acid, acetic acid and carbonate, even at low concentrations.

**1.2.3** Cross sensitivity (lack of resolution) may occur in the case of large differences in concentration between the anions determined (F, Cl, NO<sub>2</sub>, PO<sub>4</sub>, Br, NO<sub>3</sub>, SO<sub>4</sub>).

**1.2.4** The bromide and phosphate anions do not interfere in the working range specified, unless otherwise stated.

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

**1.2.6** The concentration ratios given in table 1 were checked experimentally for various representative conditions. No interferences could be observed when 50 µl of sample volume was used for the chromatographic analysis.

**1.2.7** The information in 1.2.4 to 1.2.6 is valid only as long as the quality requirements of the separating column are fulfilled (see clause 6) and the electrical conductivity of the sample is less than 1 000 µS/cm (except fluoride: < 500 µS/cm). For natural samples, the peak resolution (*R*) needs to be better than 1,3 (see figure 3).

**1.2.8** Solid material and organic compounds (e.g. mineral oils, detergents and humic acids) shorten the life-time of the separating column. They should therefore be removed from the sample prior to analysis (see clause 7).

1.2.9 Inorganic acids, such as fluoroborate acid or chlorite, may interfere with the determination.

**Table 1 — Cross sensitivity of anions**

Ratio of the mass concentrations solute/interfering ion		Maximum tolerable absolute concentration of interfering ions mg/l	
F/Cl	1:500	Sum of all ions	400
Cl/NO <sub>2</sub>	1:50	NO <sub>2</sub>	5
Cl/NO <sub>3</sub>	1:500	NO <sub>3</sub>	500
Cl/SO <sub>4</sub>	1:500	SO <sub>4</sub>	500
NO <sub>2</sub> /Cl	1:250	Cl	100
NO <sub>2</sub> /PO <sub>4</sub>	1:50	PO <sub>4</sub>	20
NO <sub>2</sub> /NO <sub>3</sub>	1:500	NO <sub>3</sub>	500
NO <sub>2</sub> /SO <sub>4</sub>	1:500	SO <sub>4</sub>	500
PO <sub>4</sub> /Cl	1:500	Cl	500
PO <sub>4</sub> /NO <sub>3</sub>	1:500	NO <sub>3</sub>	400
PO <sub>4</sub> /Br	1:100	Br	100
PO <sub>4</sub> /NO <sub>2</sub>	1:100	NO <sub>2</sub>	100
PO <sub>4</sub> /SO <sub>4</sub>	1:500	SO <sub>4</sub>	500
Br/Cl	1:500	Cl	500
Br/PO <sub>4</sub>	1:100	PO <sub>4</sub>	100
Br/NO <sub>3</sub>	1:50	NO <sub>3</sub>	100
Br/SO <sub>4</sub>	1:500	SO <sub>4</sub>	500
NO <sub>3</sub> /Cl	1:500	Cl	500
NO <sub>3</sub> /Br	1:100	Br	100
NO <sub>3</sub> /SO <sub>4</sub>	1:500	SO <sub>4</sub>	500
SO <sub>4</sub> /Cl	1:500	Cl	500
SO <sub>4</sub> /NO <sub>3</sub>	1:500	NO <sub>3</sub>	400

## 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*.

1) To be published. (Revision of ISO 5667-3:1985)

ISO 5667-2:1991, *Water quality — Sampling — Part 2: Guidance on sampling techniques*.

ISO 5667-3:—<sup>1)</sup>, *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*.

## 3 Principle

Liquid chromatographical separation of ions by means of a separating column. Use of a low capacity anion exchanger as the stationary phase, and usually aqueous solutions of salts of weak monobasic and dibasic acids as mobile phases (eluent, see 4.11). Detection by a conductivity detector (most widely used); sometimes employed in combination 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.

NOTE 2 If no suppressor device is used, the conductivity of the eluent must be as low as possible. References covering this analytical techniques are summarized in annex A.

## 4 Reagents

Use only reagents of recognized analytical grade. The water shall have an electrical conductivity of < 0,1 µS/cm 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 fluoride** (NaF).

4.5 **Sodium chloride** (NaCl).

4.6 **Sodium nitrite** (NaNO<sub>2</sub>).

4.7 **Potassium dihydrogenphosphate** (KH<sub>2</sub>PO<sub>4</sub>).

4.8 **Sodium bromide** (NaBr).

4.9 **Sodium nitrate** (NaNO<sub>3</sub>).

#### 4.10 Sodium sulfate ( $\text{Na}_2\text{SO}_4$ ).

#### 4.11 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 4.11.1.1 and 4.11.2.2 are examples only.

Prepare the eluents using degassed water. Avoid any renewed gas pick-up during operation (e.g. by helium superposition). In order to avoid the growth of bacteria or algae, store the eluent in the dark and renew every 2 d to 3 d.

##### 4.11.1 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 are used.

##### 4.11.1.1 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 4.11.1.2).

Place 25,4 g of sodium carbonate (4.2) and 25,2 g of sodium hydrogencarbonate (4.1) in a graduated flask of nominal capacity 1 000 ml, and dilute to volume with water.

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.

##### 4.11.1.2 Sodium carbonate/sodium hydrogencarbonate eluent.

The following eluent has proved to be applicable for the determination of F, Cl,  $\text{NO}_2$ ,  $\text{PO}_4$ , Br,  $\text{NO}_3$  and  $\text{SO}_4$  in a single determination.

Place 50 ml of the concentrate (4.11.1.1) in a graduated flask of nominal capacity 5 000 ml, and dilute to volume with water.

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

##### 4.11.2 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/gluconate and sodium benzoate) are used. 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 4.11.2.1. 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.

##### 4.11.2.1 Potassium hydrogenphthalate concentrate.

The addition of the following eluent concentrate to the sample has proved to be helpful for sample pretreatment and eluent preparation (4.11.2.2).

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

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.

##### 4.11.2.2 Potassium hydrogenphthalate eluent.

For the determination of F, Cl,  $\text{NO}_2$ ,  $\text{PO}_4$ , Br,  $\text{NO}_3$ , and  $\text{SO}_4$  in a single run, the following eluent, as an example, has proved to be successful.

Place 50 ml of the concentrate (4.11.2.1) in a graduated flask of nominal capacity 5 000 ml, dilute to volume with water and adjust to pH 8,5.

The solution contains 0,001 mol/l of potassium hydrogenphthalate.

#### 4.12 Stock solutions.

Prepare stock solutions of concentration 1 000 mg/l for each of the anions: F, Cl,  $\text{NO}_2$ ,  $\text{PO}_4$ , Br,  $\text{NO}_3$  and  $\text{SO}_4$ .

Dissolve the appropriate mass of each of the substances, prepared as stated in table 2, in a small quantity of water in graduated 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.

Nitrite is easily oxidized to nitrate and therefore care should be taken to ensure the stability of its concentration.

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

Table 2 — Mass portion and pretreatment for stock solutions

Anion	Salt	Pretreatment by drying <sup>1)</sup>		
		Duration h	Temperature °C	Mass of portion g
Fluoride	NaF	1	105	2,210 0
Chloride	NaCl	2	105	1,648 4
Nitrite	NaNO <sub>2</sub>	1	105	1,499 8
Orthophosphate	KH <sub>2</sub> PO <sub>4</sub>	1	105	1,433 0
Bromide	NaBr	6	105	1,287 7
Nitrate	NaNO <sub>3</sub>	24	105	1,370 7
Sulfate	Na <sub>2</sub> SO <sub>4</sub>	1	105	1,479 0

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

#### 4.12.1 Mixed standard solutions.

Depending upon requirements, prepare standard solutions of different anion composition and concentration from the stock solutions (4.12). The risk of changes in concentration caused by interaction with the vessel material increases with decreasing anion concentration. Thus, the use of polytetrafluoroethylene (PTFE) or polyethylene vessels has proved to be satisfactory for the storage of fluoride and chloride standard solutions. Experience indicates that nitrate standard solutions are more stable in borosilicate bottles.

To avoid cross contamination, always use the same vessels for the same anions and concentrations.

#### 4.12.2 Mixed standard solution I.

The mass concentrations of this solution are as follows:

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

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

Pipette the volumes given in table 3 into a graduated flask of nominal capacity 100 ml, and dilute to volume with water.

Store the solution in a polyethylene vessel. If stored at 4 °C to 6 °C, the solution is stable for about one week.

#### 4.12.3 Mixed standard solution II.

The mass concentrations of this solution are as follows:

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

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

Table 3 — Volumes of stock solutions for the preparation of the mixed standard solution I

Anion	Stock solution ml	Anion concentration mg/l
F	1	10
Cl	10	100
NO <sub>2</sub>	1	10
PO <sub>4</sub>	1	10
Br	1	10
NO <sub>3</sub>	10	100
SO <sub>4</sub>	10	100

Pipette 10 ml of the mixed standard solution I (4.12.2) into a graduated flask of nominal capacity 100 ml, and dilute to volume with water.

Store the solution in a polyethylene vessel. The solution is stable for only 1 d to 2 d, even if stored at 4 °C to 6 °C.

#### 4.12.4 Mixed standard solution III.

The mass concentrations of this solution are as follows:

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

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

Pipette, 1 ml of the mixed standard solution I (4.12.2) into a graduated flask of nominal capacity 100 ml, and dilute to volume with water.

Store the solution in a PTFE vessel. Prepare the solution on the day of use.



**4.13 Anion calibration solution.**

Depending on the anion concentration expected, use the stock solution (4.12) or the mixed standard solutions I and II (4.12.2 and 4.12.3 respectively) to prepare five to ten calibration solutions covering the expected working range as evenly as possible.

For example, proceed as follows for the range of 0,1 mg/l to 1,0 mg/l for F, NO<sub>2</sub>, PO<sub>4</sub>, Br, and 1 mg/l to 10 mg/l for Cl, NO<sub>3</sub>, SO<sub>4</sub>. Pipette into a series of graduated flasks of nominal capacity 100 ml, 1 ml, 2 ml, 3 ml, 4 ml, 5 ml, 6 ml, 7 ml, 8 ml, 9 ml and 10 ml of the mixed standard solution I (4.12.2), dilute to volume with water and add 1 ml of the eluent.

The concentrations of the calibration solutions are listed in table 4.

**4.14 Blank solutions.**

Fill a graduated flask of nominal capacity 100 ml, up to volume with water and add 1 ml of the eluent concentrate (4.11.1.1 or 4.11.2.1).

**5 Apparatus**

Usual laboratory apparatus and

**5.1 Ion chromatographic system**, complying with the quality requirements of clause 6. In general, it shall consist of the following components (see figure 1).

**5.1.1 Ion exchange chromatographic apparatus**, comprising the following:

- eluent reservoir;
- pump having a very low pulsation effect;
- sample injection system (e.g. sample loop, 50 µl);
- precolumn (see clause 7);
- separating column with the required separating performance (see clause 6);
- conductivity detector, with or without a suppressor device;
- recording device (e.g. integrator with plotter).

iTeh STANDARD PREVIEW  
(standards.iteh.ai)

ISO 10304-1:1992

<https://standards.iteh.ai/catalog/standards/sist/c9277918-24f7-4c62-a1e2-9ee1742a131b/iso-10304-1-1992>  
**Table 4 — Concentrations of the calibration solutions**

Anion	Concentrations of the calibration solutions mg/l
F	Working range 0,1 mg/l to 1,0 mg/l 0,1; 0,2; 0,3; 0,4; 0,5; 0,6; 0,7; 0,8; 0,9; 1,0
NO <sub>2</sub>	0,1; 0,2; 0,3; 0,4; 0,5; 0,6; 0,7; 0,8; 0,9; 1,0
PO <sub>4</sub>	0,1; 0,2; 0,3; 0,4; 0,5; 0,6; 0,7; 0,8; 0,9; 1,0
Br	0,1; 0,2; 0,3; 0,4; 0,5; 0,6; 0,7; 0,8; 0,9; 1,0
Cl	Working range 1,0 mg/l to 10,0 mg/l 1; 2; 3; 4; 5; 6; 7; 8; 9; 10
NO <sub>3</sub>	1; 2; 3; 4; 5; 6; 7; 8; 9; 10
SO <sub>4</sub>	1; 2; 3; 4; 5; 6; 7; 8; 9; 10
NOTE — The addition of 1ml of the eluent concentrate solution decreases the concentration of the calibration solution. However, this deviation is compensated by the equal treatment of the sample (see clause 7).	

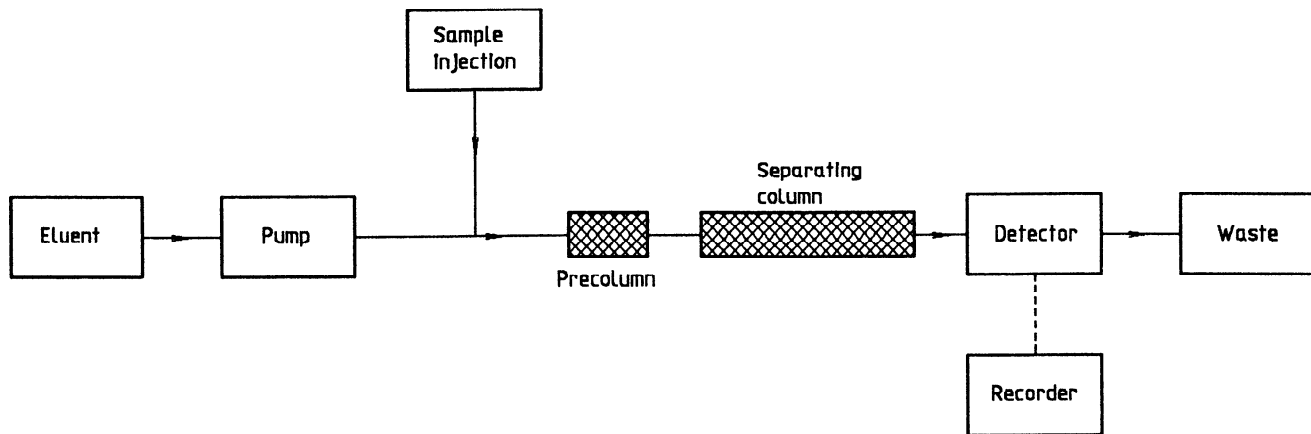


Figure 1 — Schematic diagram of an ion chromatography system

## 5.2 Additional equipment, including the following:

- drying oven;
- desiccator;
- graduated flasks, of nominal capacities 100 ml, 1 000 ml, and 5 000 ml;
- graduated flasks, of nominal capacity 100 ml, plastics, to be used for low concentrations (e.g. < 0,1 mg/l);
- graduated pipettes, of nominal capacity 1 ml to 10 ml or microlitre syringes;
- membrane filtering apparatus with membrane filters of mean pore size 0,45 µm.

Calculate the peak resolution  $R$  using the equation

$$R = \frac{2(t_{R2} - t_{R1})}{W_1 + W_2} \quad \dots (1)$$

where

$t_{R1}$  is the retention time, in seconds, of the 1<sup>st</sup> peak;

$t_{R2}$  is the retention time, in seconds, of the 2<sup>nd</sup> peak;

$W_1$  is the peak width, in seconds, of the 1<sup>st</sup> peak;

$W_2$  is the peak width, in seconds, of the 2<sup>nd</sup> peak.

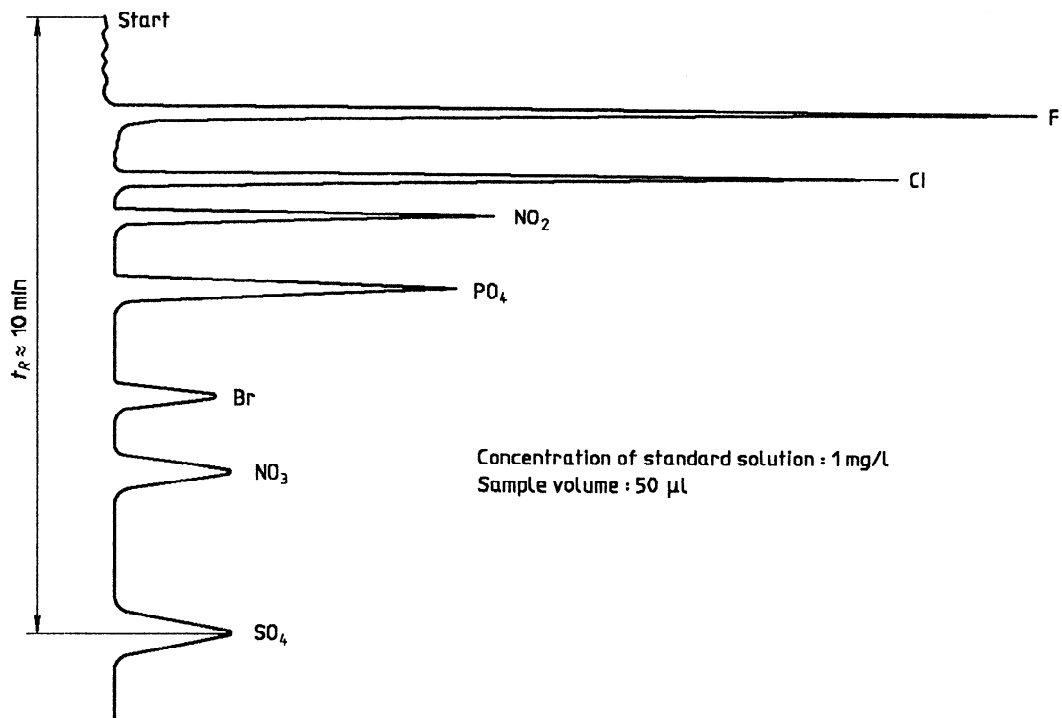
## 6 Quality requirements of the separating column

The separating column is the essential part of the ion chromatographic system. Its separating performance depends on several operating factors, such as column material and type of eluents. Within the scope of this part of ISO 10304, use only those separating columns that yield a baseline resolved separation of all the components of the injected standard solution containing seven anions (F, Cl, NO<sub>2</sub>, PO<sub>4</sub>, Br, NO<sub>3</sub>, and SO<sub>4</sub>), at a concentration level of 1 mg/l, (see figure 2). If only some of the anions shown in figure 2 have to be determined, this requirement is applicable for those anions. Therefore, the peak resolution shall not fall below  $R = 1,3$  (see equation 1 and figure 3).

## 7 Sampling and sample pretreatment

Use vessels made of polytetrafluoroethylene (PTFE) or polyethylene for sampling. Use only new vessels or those that have been rinsed thoroughly with water (see clause 4). To prevent the risk of contamination of the sample, do not use strong mineral acids or alkaline detergent solutions for cleaning the vessels.

After the arrival of the sample in the laboratory, filter it through a membrane filter (of pore size 0,45 µm) to prevent adsorption of the anions on particulate matter or conversion of anions by bacterial growth. Prevent the risk of contamination of the sample by the membrane (e.g. filter the sample and discard the first portion of the filtrate).



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

ITeH STANDARD PREVIEW  
(standards.iteh.ai)

Figure 2 — Example of a chromatogram of a column conforming to this part of ISO 10304

ISO 10304-1:1992

<https://standards.iteh.ai/catalog/standards/sist/c9277918-24f7-4c62-a1e2-9eef742a31b/iso-10304-1-1992>

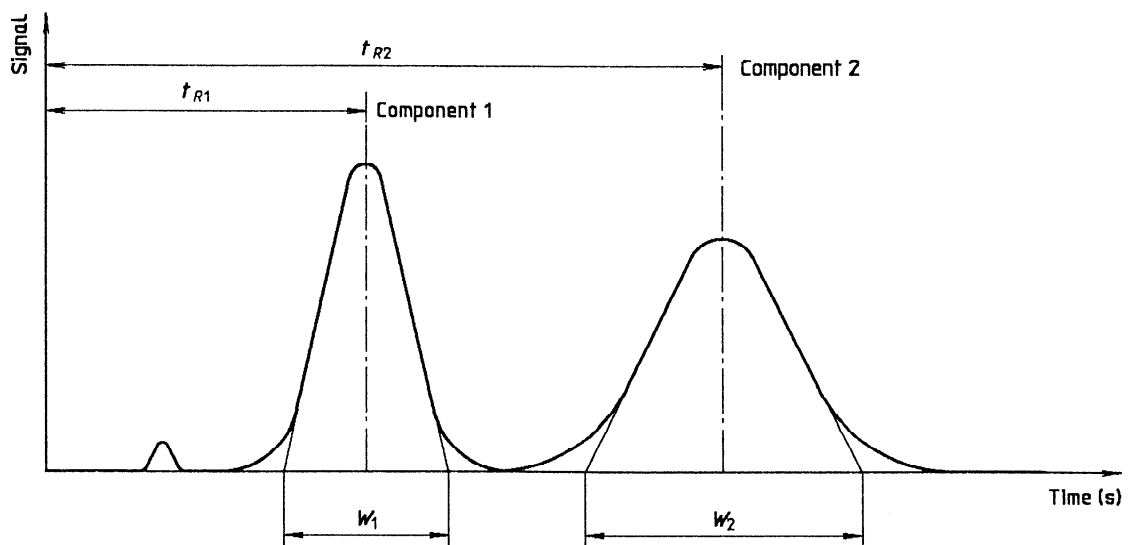


Figure 3 — Idealized representation of the chromatographic separation