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

Part 3:
Determination of chromate, iodide, sulfite, thiocyanate and thiosulfate

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

Partie 3: Dosage des ions chromate, iodure, sulfite, thiocyanate et thiosulfate

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Contents

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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.

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 10304-3 was prepared by Technical Committee ISO/TC 147, *Water quality,* SC 2, *Physical, chemical and 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 1: Determination of fluoride, chloride, bromide, nitrate, nitrite, orthophosphate and sulfate in water with low contamination*
- *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*

Annexes A and B of this part of ISO 10304 are for information only.

Introduction

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

a) Resolution of the column:	For the anion to be determined it is essential that the peak resolution does not fall below $R = 1,3$ (4.2.2, figure 3)
b) Method of detection:	1) measurement of the electrical conductivity with or without suppressor device 2) spectrometric measurement (UV/VIS), directly or indirectly 3) amperometric direct detection
c) Applicability of the method:	Working ranges according to table 1
d) Calibration (4.5.1):	Calibration and determination of the linear working range (see ISO 8466-1)
Guaranteeing the analytical quality:	Validity check of the calibration function. Replicate determinations if necessary.

The diversity of the appropriate and suitable assemblies and the procedural steps depending on them permit a general description only.

For further information on the analytical technique, see reference [1].

Water quality – Determination of dissolved anions by liquid chromatography of ions – Part 3: Determination of chromate, iodide, sulfite, thiocyanate and thiosulfate

1 Scope

This part of ISO 10304 specifies methods for the determination in aqueous solution of the dissolved anions
- iodide, thiocyanate and thiosulfate (clause 4);
- sulfite (clause 5);
- chromate (clause 6).

An appropriate pretreatment of the sample (e.g. dilution) and the application of a conductivity detector (CD), UV detector (UV) or amperometric detector (AD) make the working ranges given in table 1 feasible.

Table 1 — Applicable working ranges

Anion	Working range [1])	Detector
Chromate (CrO_4), clause 6	0,05 mg/l to 50 mg/l	UV (λ = 365 nm)
Iodide (I), clause 4	0,1 mg/l to 50 mg/l	CD or UV (λ = 205 nm to 236 nm) AD (approximately 0,7 V to 1,1 V)
Sulfite (SO_3), clause 5	0,1 mg/l to 50 mg/l 0,5 mg/l to 50 mg/l	CD UV (λ = 205 nm to 220 nm)
Thiocyanate (SCN), clause 4	0,1 mg/l to 50 mg/l	CD or UV (λ = 205 nm to 220 nm) AD (approximately 0,7 V to 1,1 V)
Thiosulfate (S_2O_3), clause 4	0,1 mg/l to 50 mg/l	CD or UV (λ = 205 nm to 220 nm) AD (approximately 0,7 V to 1,1 V)

[1]) The working range is restricted by the exchange capacity of the columns. Dilute the sample into the working range if necessary.

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 International Standard 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.*
ISO 10304-2:1995	*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.*

3 Principle

3.1 Separation of ions is carried out by liquid chromatography using a separating column. A low capacity anion exchanger is used as the stationary phase, and usually aqueous solutions of salts of weak monobasic and dibasic acids as mobile phases (eluent, see 4.1.16, 5.1.4, 6.1.9).

3.2 The addition of organic agents, such as 4-hydroxybenzonitrile (see 4.1.16.2.2, 4.3.4), or organic solvents to the eluent can be used to speed up the elution or reduce the tailing effects, especially for the analysis of the more strongly polarizable ions iodide, thiocyanate and thiosulfate.

3.3 Detection is by conductivity (CD), UV and amperometric detectors (AD).

3.3.1 When using conductivity detectors it is essential that the eluents have a sufficiently low conductivity. For this reason, conductivity detectors are often combined with suppressor devices (cation exchangers) which will reduce the conductivity of the eluents and transform the sample species into their respective acids.

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

3.3.3 Amperometric detectors measure the quantity of current caused by the oxidation of anions. The oxidation voltage required for the anions in question depends on the pH value of the eluent.

3.4 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).

4 Determination of iodide, thiocyanate and thiosulfate

Follow the instructions given in clause 4 to make the working ranges given in table 1 feasible.

4.1 Reagents

Use only reagents of recognized analytical grade, if commercially available. Carry out weighing with an accuracy of 1% of the nominal mass. The water shall have an electrical conductivity of < 0,01 mS/m and shall not contain particulate matter of a particle size > 0,45 µm. An increase of the electrical conductivity due to an uptake of carbon dioxide does not interfere with the determination.

4.1.1 Sodium hydrogen carbonate, $NaHCO_3$

4.1.2 Sodium carbonate, Na_2CO_3

4.1.3 Phthalic acid, $C_8H_6O_4$

4.1.4 Disodium tetraborate, $Na_2B_4O_7$

4.1.5 Gluconic acid, sodium salt, $C_6H_{11}NaO_7$

4.1.6 Methanol, CH_3OH

4.1.7 Boric acid, H_3BO_3

4.1.8 Glycerol, $C_3H_8O_3$

4.1.9 Acetonitrile, CH_3CN

4.1.10 Sodium hydroxide solution, $c(NaOH) = 0,1$ mol/l

4.1.11 4-hydroxybenzonitrile, C_7H_5NO

4.1.12 Tris(hydroxymethyl)aminomethane, $C_4H_{11}NO_3$

4.1.13 Sodium thiosulfate, pentahydrate, $Na_2S_2O_3 . 5 H_20$

4.1.14 Sodium iodide, NaI

4.1.15 Potassium thiocyanate, KSCN

4.1.16 Eluents

4.1.16.1 General

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 4.1.16.2 and 4.1.16.3 are examples only.

A selection of reagents for some commonly used eluents is presented in 4.1.1 to 4.1.12.

Degas all eluents or prepare eluents using degassed water (4.1). Take steps to avoid any renewed gas pick-up during operation (e.g. by helium superposition). In order to minimize the growth of bacteria or algae, store eluents in the dark and renew every 2 to 3 days.

4.1.16.2 Examples of eluents for ion chromatography using the suppressor technique

For the application of the suppressor technique, sodium hydroxide and solutions of salts of weakly dissociated acids, such as sodium carbonate/sodium hydrogen carbonate, sodium hydrogen carbonate, and sodium tetraborate are used.

4.1.16.2.1 Sodium carbonate/sodium hydrogen carbonate concentrate

The addition of the following eluent concentrate to the sample has proved to be successful for sample pretreatment and eluent preparation (see 4.1.16.2.2).

- Place 36 g of sodium carbonate (4.1.2) and 36,1 g of sodium hydrogen carbonate (4.1.1) in a graduated flask of nominal capacity 1 000 ml, and dilute to volume with water (4.1).

The solution contains 0,34 mol/l of sodium carbonate and 0,43 mol/l of sodium hydrogen carbonate. This solution is stable for several months if stored at 4 °C to 6 °C.

4.1.16.2.2 Sodium carbonate/sodium hydrogen carbonate eluent

The following eluent has proved to be applicable for the determination of iodide, thiocyanate, thiosulfate:

- Place 50 ml of the concentrate (4.1.16.2.1) in a graduated flask of nominal capacity 5 000 ml, add water (4.1), add 750 mg of 4-hydroxybenzonitrile (4.1.11) and dilute to volume with water (4.1) [1][2].

The solution contains 0,0034 mol/l of sodium carbonate, 0,0043 mol/l of sodium hydrogen carbonate and 0,0013 mol/l of 4-hydroxybenzonitrile. Renew the eluent every 2 to 3 days (4.1.16).

The concentrations of iodide, thiocyanate and thiosulfate in these calibration solutions are 1 mg/l, 2 mg/l, 3 mg/l, 4 mg/l, 5 mg/l, 6 mg/l, 7 mg/l, 8 mg/l, 9 mg/l and 10 mg/l respectively.

Prepare the calibration solutions on the day of use.

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1) 4-hydroxybenzonitrile can be added to speed up the elution or reduce the tailing effects, for the analysis of iodide, thiocyanate and thiosulfate (4) but it can cause interferences with the determination of iodide, thiocyanate and thiosulfate when the UV detector is used (4.3.4).

2) To improve the solubility of 4-hydroxybenzonitrile the substance can be dissolved in a small quantity of methanol or ethanol and, after addition to the eluent concentrate the solution should be stirred overnight.

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

For ion chromatography without suppressor devices, use salt solutions, e.g. potassium hydrogenphthalate, 4-hydroxybenzoate, sodium borate/gluconate, and sodium benzoate. The concentration of the salts is usually in the range of 0,0005 to 0,01 mol/l. Concentrate and eluent solutions are prepared as described in 4.1.16.2.1 or 4.1.16.2.2 respectively.

4.1.16.3.1 Phthalic acid concentrate

The addition of the following eluent concentrate to the sample has proved to be successful for sample pretreatment and eluent preparation (see 4.1.16.3.2).

- Place 4,485 g of phthalic acid (4.1.3) in a graduated flask of nominal capacity 1 000 ml, dissolve in approximately 800 ml of water (4.1), add 100 ml of acetonitrile (4.1.9) and dilute to volume with water (4.1). Adjust to a pH of 4 with tris(hydroxymethyl)aminomethane (4.1.12; can be added either in solid form or as solution, e.g. 1 mol/l).

The solution contains 0,027 mol/l phthalic acid and approximately 10 % of acetonitrile.

4.1.16.3.2 Phthalic acid eluent

The following eluent can be used for the determination of iodide, thiocyanate and thiosulfate:

- Pipette 100 ml of the concentrate (4.1.16.3.1) into a graduated flask of nominal capacity 1 000 ml and dilute to volume with water (4.1).

The solution contains 0,0027 mol/l of phthalic acid and approximately 1 % of acetonitrile. The pH of the solution should be in the range of 4,0 to 4,5 [3]. Renew the eluent every 2 to 3 days (4.1.16).

4.1.16.3.3 Borate/gluconate concentrate

The following eluent concentrate has proved useful for the preparation of the eluent (4.1.16.3.4) and the pretreatment of the samples.

- Weigh 16 g of gluconic acid, sodium salt (4.1.5), 18 g of boric acid (4.1.7), and 25 g of disodium tetraborate (4.1.4) into a graduated flask, nominal capacity 1 000 ml, dissolve in approximately 500 ml of water (4.1), add 250 ml of glycerol (4.1.8) and dilute to volume with water (4.1).

The solution contains 0,073 mol/l of gluconic acid, 0,291 mol/l of boric acid, 0,124 mol/l of disodium tetraborate, and approximately 25 % of glycerol. The solution is stable for several months if stored at 4 °C to 6 °C.

4.1.16.3.4 Borate/gluconate eluent

The following eluent can, for example, be used for the determination of iodide, thiocyanate and thiosulfate.

- Place 500 ml of water (4.1) in a graduated flask of nominal capacity 1 000 ml, add 23,5 ml of the concentrate (4.1.16.3.3), 120 ml of acetonitrile (4.1.9) and dilute to volume with water (4.1).

The solution contains 0,0017 mol/l of gluconic acid, 0,0068 mol/l of boric acid, 0,0029 mol/l of disodium tetraborate, approximately 0,6 % of glycerol, and approximately 12 % of acetonitrile. The pH of this solution should be in the range of 8.3 to 8.7 [4]. Renew the eluent every 2 to 3 days (4.1.16).

4.1.17 Stock solutions

Prepare stock solutions of concentration 1 000 mg/l for each of the anions iodide, thiocyanate and thiosulfate.

- 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 in polyethylene bottles.

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

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[3] pH values $<4{,}0$ or $>4{,}5$ can increase retention times or cause a peak resolution $R < 1{,}3$ (for criteria for R see 4.2.2).

[4] pH values $<8{,}3$ or $>8{,}7$ can increase retention times or cause a peak resolution $R < 1{,}3$ (for criteria for R see 4.2.2).

Table 2 — Mass portion and pretreatment for stock solutions

		Pretreatment by drying1)		
Anion	**Salt**	**Duration** **h**	**Temperature** **°C**	**Mass of portion** **g/l**
Iodide	NaI	3	103 to 106	1,1812
Thiocyanate	KSCN	1	103 to 106	1,6732
Thiosulfate 2)	$Na_2S_2O_3 \cdot 5H_2O$	Do not dry		2,2134

1) Let the substance cool in a sealed desiccator after drying.
2) Titre adjustment is necessary prior to use.

4.1.18 Mixed standard solutions

Depending upon the concentrations expected, prepare standard solutions of different anion composition and concentration from the stock solutions (4.1.17). The risk of changes in concentration caused by interaction with the vessel material increases with decreasing anion concentration. Store the standard solutions in polyethylene vessels.

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

4.1.18.1 Iodide, thiocyanate, thiosulfate mixed standard solution I

The mass concentration of this solution is as follows:

ρ (I, SCN, S_2O_3) = 100 mg/l

– Pipette 10 ml each of the stock standard solution, prepared as described, in 4.1.17 into a graduated flask of nominal capacity 100 ml and dilute to volume with water (4.1).

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

4.1.18.2 Iodide, thiocyanate, thiosulfate mixed standard solution II

The mass concentration of this solution is as follows:

ρ (I, SCN, S_2O_3) = 10 mg/l

– Pipette 10 ml of mixed anion standard solution I (4.1.18.1) into a graduated flask of nominal capacity 100 ml and dilute to volume with water (4.1).

The solution is stable for only 1 to 2 days, even if stored at 4 °C to 6 °C.

Prepare further standard solutions by appropriate dilutions of mixed standard solution I (4.1.18.1).

4.1.19 Anion calibration solutions

Depending on the anion concentration expected, use the stock solution (4.1.17) or the mixed standard solutions (4.1.18.1 and 4.1.18.2) to prepare 5 to 10 calibration solutions covering the expected working range as evenly as possible.

For example, proceed as follows for the range 1,0 mg/l to 10 mg/l for the anions iodide, thiocyanate and thiosulfate.

– Into a series of graduated flasks of nominal capacity 100 ml, pipette 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 (4.1.18.1), dilute to volume with water and add 0,1 ml of the sodium hydroxide solution5)6) (4.1.10).

4.1.20 Blank solution

Fill a graduated flask of nominal capacity 100 ml, up to volume with water and add 0,1 ml of sodium hydroxide solution (4.1.10)5)6).

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5) Alternatively, use the eluent concentrate according to 4.1.16.2.1 or 4.1.16.3.3.

6) The addition of 0,1 ml of sodium hydroxide solution or 0,1 ml of eluent concentrate will reduce the concentration of the reference solution. This effect is compensated for by the equal treatment of the sample.

4.2 Apparatus

Usual laboratory apparatus and

4.2.1 Ion chromatography system, complying with the quality requirements of 4.2.2. In general it shall consist of the following components (see figure 1):

4.2.1.1 Ion chromatography apparatus, comprising

- eluent reservoir;
- pump, suitable for HPLC;
- sample injection system incorporating a sample loop (e.g. sample loop of volume 50 µl);
- precolumn (see 4.5.2) containing e.g. the same resin material as the analytical separator column or packed with a macroporous polymer;
- separator column with the specified separating performance (4.2.2);
- conductivity detector (with or without a suppressor device assembly) or UV detector (e.g. spectrophotometer; 190 nm to 400 nm) or amperometric detector;
- Recording device (e.g. recorder, integrated with printer).

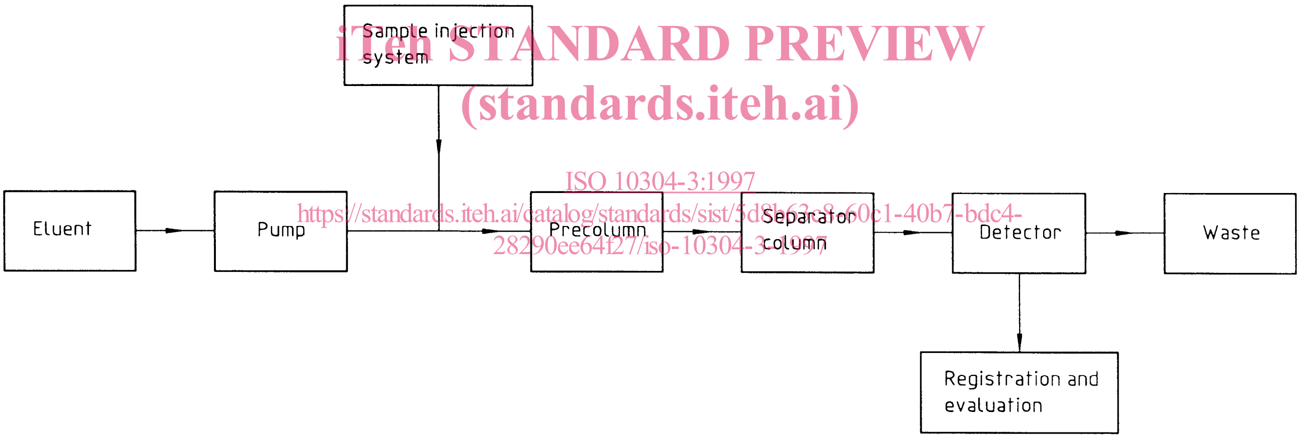
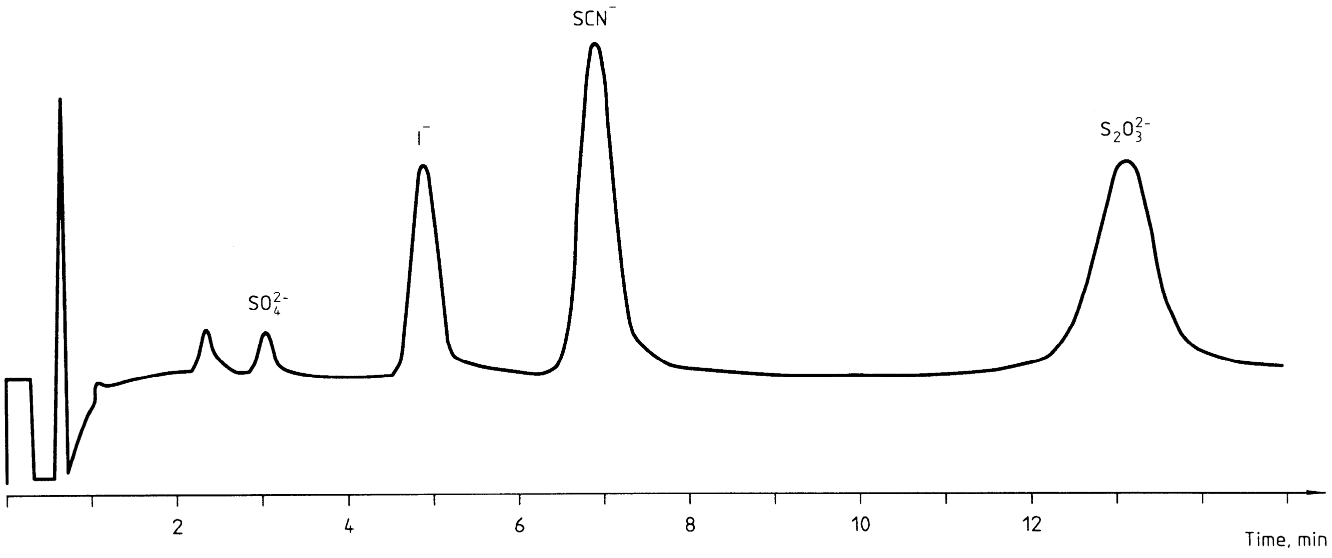


Figure 1 — Schematic representation of an ion chromatography system

4.2.2 Quality requirements for the separator column

The separator column is the essential part of the ion chromatographic system. Its separation performance depends on several operating factors, such as column material and type of eluent. Within the scope of this standard, use only those separator columns that yield a baseline-resolved separation of all the components of the injected ions (e.g. iodide, thiocyanate and thiosulfate; see figure 2) at a concentration level of 1 mg/l each. If only some of the anions shown in figure 2 have to be determined, this requirement is applicable to those anions. For chromatograms of samples and standard solutions of higher concentrations, the resolution to the nearest (interfering) peak (see figure 3) shall not fall below $R = 1{,}3$ [see equation (1)].



NOTE: Elution sequence and retention times can vary, depending on the type of column and composition of the eluent.

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

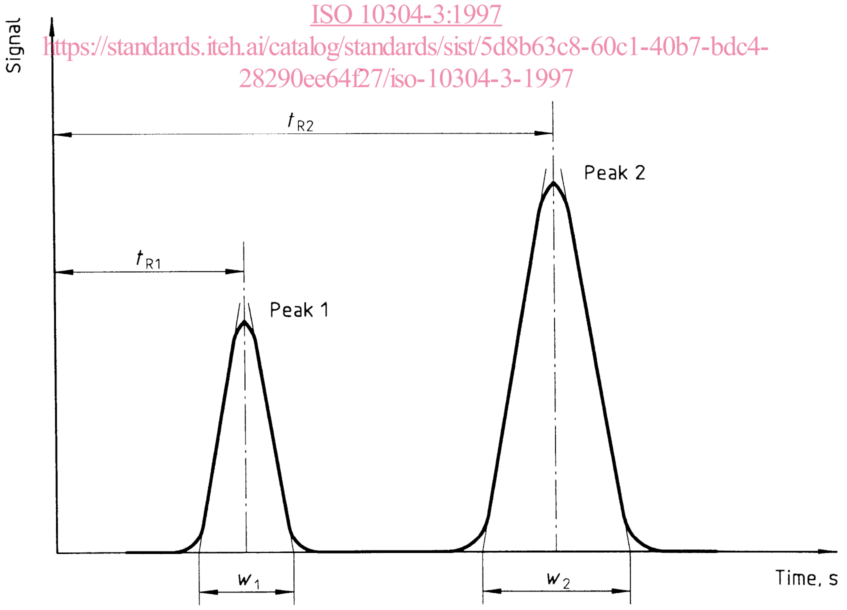


Figure 3 — Graphical representation of the parameters to calculate the peak resolution R