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ISO 10304-3

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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.

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 drying[1])				
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])	$Na_2S_2O_3 . 5H_2O$	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:

$$\rho (I, SCN, S_2O_3) = 100 \text{ mg/l}$$

– 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:

$$\rho (I, SCN, S_2O_3) = 10 \text{ mg/l}$$

– 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 solution[5])[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).

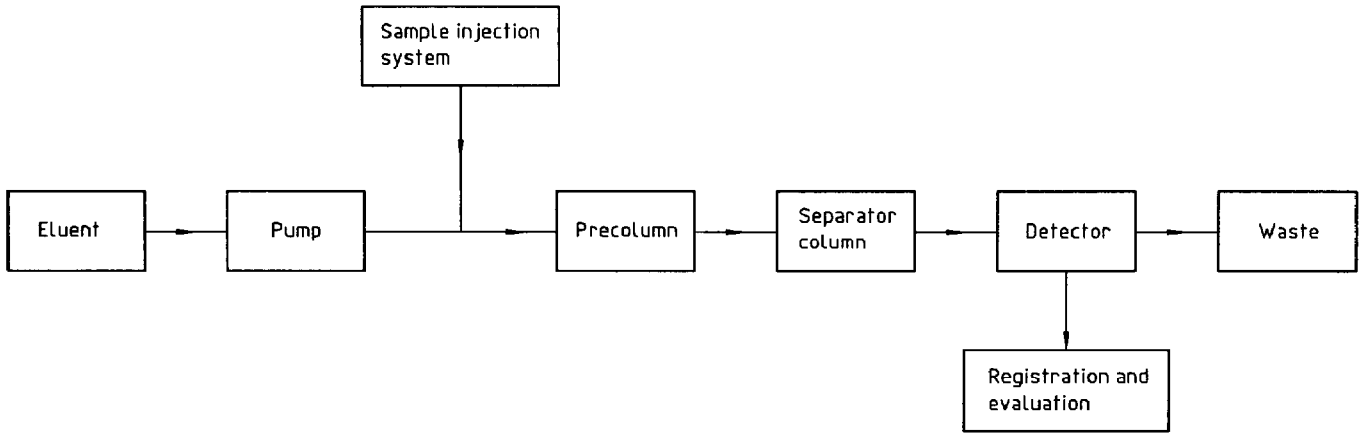
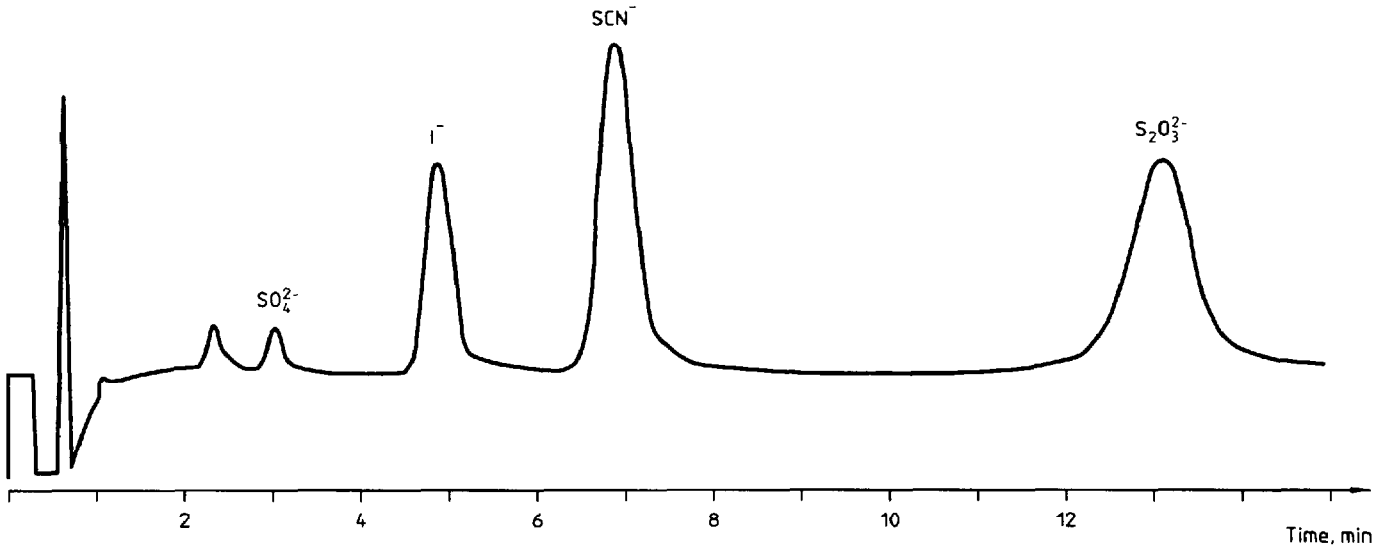


Figure 1 — Schematic representation of an ion chromatography system

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

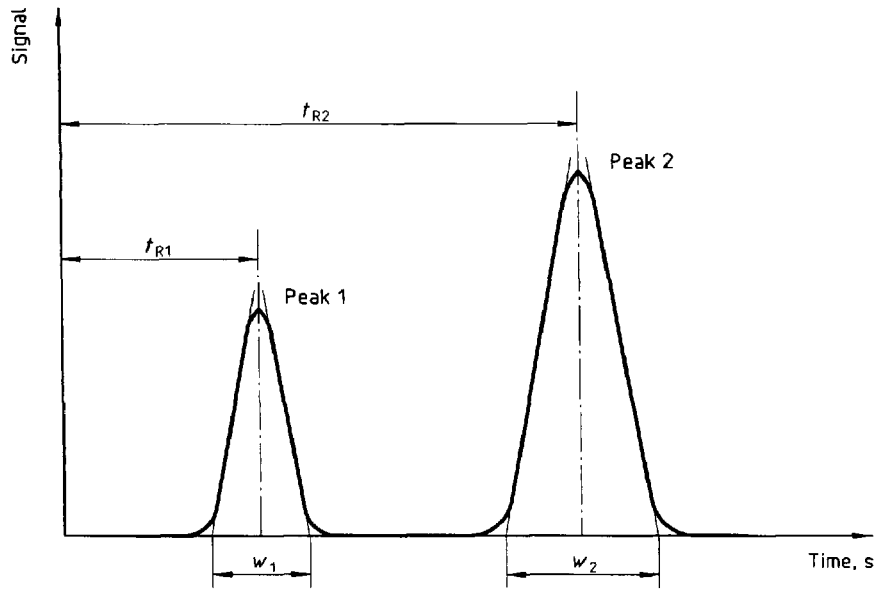


Figure 3 — Graphical representation of the parameters to calculate the peak resolution *R*

Calculate the peak resolution R using equation (1):

$$R_{2,1} = \frac{2\,(t_{R2} - t_{R1})}{(w_2 + w_1)} \quad \text{...(1)}$$

where

$R_{2,1}$ is the resolution for the peak pair 2,1;
t_{R1} is the retention time, in seconds, of peak 1;
t_{R2} is the retention time, in seconds, of peak 2;
w_1 [7]) is the peak width, in seconds, on the time axis of peak 1;
w_2 [7]) is the peak width, in seconds, on the time axis of peak 2.

4.2.3 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 and made of 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;
- cartridges or columns with non-polar phases (e.g. RP C18 or polyvinylpyrrolidone respectively) to be used for sample preparation;
- cation exchanger in the Ba-form (cartridge);
- cation exchanger in the H-form (cartridge).

4.3 Interferences

4.3.1 Organic acids, such as mono- or dicarboxylic acids, can interfere.

4.3.2 Cross-sensitivities (lack of resolution) in the determination of thiocyanate and thiosulfate are observed rarely, even in the case of large differences in concentration between the anions.

4.3.3 The presence of sulfate can cause interference with the determination of iodide. Remove sulfate with the aid of special exchangers (4.4.2).

4.3.4 The presence of organic agents in the eluent (3.2 and 4.1.16.2.2) can cause interferences with the determination of e.g. iodide, thiocyanate or thiosulfate when the UV detector is used.

4.3.5 Solid material and organic compounds (such as mineral oils, detergents, and humic acids) shorten the lifetime of the separator column. They should therefore be eliminated from the sample prior to analysis (4.4.1.6 and 4.4.1.8).

7) w_1, w_2 are the base widths of the equilateral triangle constructed representing four times the standard deviation of the Gaussian peak.

4.4 Sampling and sample pretreatment

4.4.1 General requirements

4.4.1.1 It is important that the laboratory receive a sample which is truly representative and has not been damaged or changed during transport or storage. Sampling is not part of the method specified in this part of ISO 10304.

4.4.1.2 Use clean glass or polyethylene vessels for sampling.

4.4.1.3 After sample collection adjust the pH of the samples with sodium hydroxide solution[8)][9)] (4.1.10) to approximately pH 10 (e.g. 1 ml of sodium hydroxide per 1 l of sample). In case of strongly acid waste water samples use concentrated sodium hydroxide solution.

4.4.1.4 After arrival of the sample in the laboratory filter it through a membrane filter (of pore size 0,45 µm), to prevent further adsorption of the anions on particulate matter or conversion of anions by bacterial growth.

4.4.1.5 If an immediate analysis is not feasible, stabilize the membrane-filtered sample by cooling (4 °C to 6 °C) or deep-freezing (-16 °C to -20 °C), provided this procedure will not impair the results (see ISO 5667, all parts).

4.4.1.6 Prior to injection into the analyser, filter the sample again through a membrane filter (of pore size 0,45 µm) to remove any particulate matter, if present. Prevent the risk of precipitate formation during analysis[10)].

4.4.1.7 Prevent the risk of contamination of the sample from the membrane (e.g. rinse the membrane with a small amount of the sample itself and discard the first portion of the filtrate).

4.4.1.8 Waters strongly contaminated with organic compounds can damage the separator column. In this case it is advisable to dilute the sample and to filter it via a non-polar phase (e.g. RP C18 or polyvinylpyrrolidone, 4.2.3) before injection (4.5.2).

4.4.1.9 Treat blank solution (4.1.20) and calibration solutions (4.1.19) in the same manner as the sample solutions.

4.4.1.10 Continue with 4.4.2, if sulfate interferes with the determination of iodide.

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

9) 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.

10) To avoid precipitation reactions caused by changing pH values: check the sample pH prior to injection, adjust the pH of the sample to the pH of the eluent, if necessary (see 4.4.1.3), continue with 4.4.1.7.

4.4.2 Sample pretreatment in order to avoid interference with sulfate

To avoid separation problems with the elution of sulfate near to iodide proceed as follows:

- Dilute the sample, if necessary, and run it through a strongly acid cation exchanger in the H-form (cartridge[11]), 4.2.3).
- Run the filtrate through a cation exchanger in the Ba-form (cartridge[11]), 4.2.3) to remove dissolved sulfate ions from the sample.
- Run the filtrate through a cation exchanger in the H-form (cartridge[11]), 4.2.3) to remove dissolved barium ions from the eluate.
- Treat the blank solution (4.1.20) and calibration solutions (4.1.19) in the same manner.

4.5 Procedure

Set up the ion chromatograph according to the instrument manufacturer's instructions (e.g. the instrument is ready for operation as soon as the baseline is stable). Perform the calibration as described in 4.5.1. Measure samples and blank solution (4.1.20) as described in 4.5.2.

4.5.1 Calibration

Inject the calibration solutions. Identify the peaks for particular anions by comparing the retention times with those of the standard solutions (see 4.1.18.1 or 4.1.18.2) according to the manufacturer's information. Take into account the fact that the retention times can be dependent on concentration and matrix. In calculating concentrations, use the characteristic that the area (or height) of the peak (signal) is proportional to the concentration of the anion.

When the analytical system is first evaluated, and at intervals afterwards, establish a calibration function (see ISO 8466-1) for the measurement as follows.

4.5.1.1 Prepare calibration solutions as described in 4.1.19.

4.5.1.2 Analyse the calibration solutions chromatographically.

4.5.1.3 Use the data obtained to calculate the regression line. Reject if it is not linear (for linearity criteria, refer to ISO 8466-1). The following equation (calibration function) applies for the ion i to be determined:

$$y_i = b_i \rho_i + a_0 \qquad \text{...(2)}$$

where:

y_i is the measured value (size of signal), in terms of peak height or peak area respectively, in millimetres or microvolt seconds;

b_i is the slope of the calibration function, e.g. mm · l/mg; µV · s · l/mg;

ρ_i is the mass concentration, in milligrams per litre, of the ion i;

a_0 is the ordinate intercept of the calibration function (calculated blank), e.g. mm, µV · s.

4.5.1.4 Subsequently, check the continuing validity of the established calibration function (4.5.2.1).

11) Before use rinse the cartridge with water (4.1).

4.5.2 Measurement of samples using the standard calibration procedure

4.5.2.1 Procedure

After establishing the calibration function, inject the pretreated sample (4.4) into the chromatograph and measure the peaks as above (4.5).

Generally, the use of a precolumn is strongly recommended, especially for the injection of waters strongly contaminated with organic compounds (4.4.1.8). This serves to protect the analytical separator column. In general, two different types of precolumn can be used: those containing the same resin material as the analytical separator column and those packed with a macroporous polymer (4.2.3).

If the ion concentration of the sample to be analysed exceeds the calibration range, dilute the sample and analyse it. Sometimes it may be necessary to establish a separate calibration function for the lower concentration range.

If matrix interferences are to be expected, use the method of standard addition to safeguard the results (verify the peaks by comparing the retention times of the spiked sample with those of the orignial sample).

Measure the blank solution (4.1.20) in the same manner.

4.5.2.2 Validity check of the calibration function

In order to verify the continuing validity of the calibration function, measure a minimum of two calibration solutions of different concentrations in the lower and upper parts of the working range. This should take place after the set up procedure (4.5) and after each sample series at least, but in any case after 10 to 20 measurements (4.5.2).

Calculate the mass concentrations of the analysed calibration solutions using the inverse calibration function [see 4.6, equation (3)]. The concentrations need to be in the range of the confidence band. If the calibration function is not valid, carry out a new calibration (see 4.5.1).

4.6 Calculation

Estimate the mass concentration, ρ_i, in milligrams per litre, of the anion in the solution using the peak areas or peak heights and the inverse calibration equation (2) (see 4.5.1) as follows:

$$\rho_i = \frac{y_i - a_0}{b_i} \qquad \text{...(3)}$$

For an explanation of the variables, see equation (2).

Take into account all dilution steps.

4.7 Expression of results

Report the results to a maximum of two significant figures.

EXAMPLE

Iodide (I^-)	$1{,}5 \times 10^3$	mg/l
Thiosulfate ($S_2O_3^{2-}$)	12	mg/l
Thiocyanate (SCN^-)	1,1	mg/l

4.8 Test report

The test report shall contain the following information:

a) a reference to this part of ISO 10304;

b) identity of the water sample;

c) expression of the results according to 4.7;

d) description of the sample pretreatment, if relevant;

e) description of the chromatographic conditions: Type of instrument and column, column dimensions, eluent flow rate, type of detector and detector parameters;

f) description of the method used for the evaluation (peak height or peak area);

g) any deviation from this method and information on all circumstances which have influenced the result.

5 Determination of sulfite

Follow the instructions given in clause 5 to make the working ranges given in table 1 feasible.

5.1 Reagents

In addition to the reagents mentioned in 4.1, the following reagents shall be used.

5.1.1 Sodium sulfite, Na_2SO_3

5.1.2 Formaldehyde, (CH_2O), 37 % (*V/V*) aqueous solution

5.1.3 Aluminium hydroxide, $Al(OH)_3 \cdot x\,H_2O$ (min. 50% Al_2O_3)

5.1.4 Eluents

The general remarks of 4.1.16.1 on suitability and composition of mobile phases remain valid for the determination of sulfite. Obtain the exact composition of the eluents from the column manufacturer's instructions.

A selection of reagents for some commonly used eluents is given in 4.1.1 to 4.1.12 and 5.1.

5.1.4.1 Examples of eluents for ion chromatography using the suppressor technique

See also 4.1.16.2.

5.1.4.1.1 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 5.1.4.1.2)

- Place 21,2 g of sodium carbonate (4.1.2) and 6,3 g of sodium hydrogen carbonate (4.1.1) into a graduated flask of nominal capacity 1 000 ml and dilute to volume with water (4.1).

The solution contains 0,2 mol/l of sodium carbonate and 0,075 mol/l of sodium hydrogen carbonate. The solution is stable for several months if stored at 4 °C to 6 °C.

5.1.4.1.2 Sodium carbonate/sodium hydrogen carbonate eluent

The following eluent has proved useful for the determination of sulfite:

– Pipette 50 ml of the concentrate (5.1.4.1.1) into a graduated flask of nominal capacity 5 000 ml, and dilute to volume with water (4.1).

The solution contains 0,002 mol/l of sodium carbonate and 0,000 75 mol/l of sodium hydrogen carbonate. Renew the eluent every 2 to 3 days (4.1.16).

5.1.4.2 Examples of eluents for ion chromatography without using suppressor technique

See also 4.1.16.3.

5.1.4.2.1 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 5.1.4.2.2).

– Dissolve with heating 4,485 g of phthalic acid (4.1.3) in approximately 200 ml of water. Add 100 mg of aluminium hydroxide (5.1.3) and boil to dissolve. Cool and add 100 ml of acetonitrile (4.1.9), transfer into a graduated flask of nominal capacity 1 000 ml and dilute to volume with water (4.1). Adjust the pH to 3,8 by adding tris(hydroxymethyl)aminomethane (4.1.12; to be added either in solid form or as solution, e.g. 1 mol/l).

The solution contains 0,027 mol/l of phthalic acid and approximately 10 % of acetonitrile. This solution is stable for several months if stored at 4 °C to 6 °C.

5.1.4.2.2 Phthalic acid eluent

The following eluent can, for example, be used for the determination of sulfite.

– Pipette 200 ml of the concentrate (5.1.4.2.1) into a graduated flask of nominal capacity 2000 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[12]). Renew the eluent every 2 to 3 days (4.1.16).

5.1.4.3 Borate/gluconate concentrate and eluent

The compositions for the concentrate or the eluent as described in 4.1.16.3.3 and 4.1.16.3.3 respectively can also be used for the determination of sulfite.

5.1.5 Sulfite standard stock solution

Prepare the stock solution of mass concentration of approximately 1 000 mg/l (SO_3) as follows.

– Transfer into a graduated flask of nominal capacity 1 000 ml, approximately 800 ml of degassed water (e.g. prepared by purging with nitrogen or helium) and add 1 ml of sodium hydroxide solution (4.1.10). Dissolve approximately 1,6 g of sodium sulfite[13]) (5.1.1) in this solution, and dilute to volume with water (4.1).
– Calibrate the freshly prepared solution immediately after preparation by an iodometric titration[14]).
– Add formaldehyde solution (5.1.2) quickly to the remaining solution (in the ratio of 1 part of formaldehyde to 1 000 parts of stock solution).

---

12) 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).

13) The salt often contains some sulfate and is stable in dry air up to temperatures of > 100 °C. Low concentrated sulfite solutions will quickly react with atmospheric oxygen. The solution is therefore made alkaline and stabilized by the addition of formaldehyde solution.

14) The iodometric titration of sulfite is subject to interference by formaldehyde. Calibrate the sulfite content before adding formaldehyde solution.

Prepare the solution on the day of use.

Alternatively use commercially available stock solution or a solution formed from hydroxymethane sulfonic acid of the required concentration. Prepare the solution according to 5.1.6.1 if necessary.

5.1.6 Standard solutions

5.1.6.1 General remarks

When preparing the sulfite standard solution (5.1.6.2) or the sulfite calibration solutions respectively (5.1.7) always add the reagents in the following sequence:

1) water
2) sodium hydroxide solution
3) formaldehyde solution
4) sodium sulfite stock solution, or sodium sulfite standard solution respectively.

Prepare the standard solutions, in the concentrations required, from the standard stock solution (3.1.5) when needed.

The lower the anion concentration, the higher the danger of alterations in concentration caused by interaction with the vessel material or reaction with atmospheric oxygen. The standard solutions shall be stored in polyethylene vessels. Always use the same vessels for the same concentration ranges in order to avoid the danger of cross-contamination.

5.1.6.2 Sulfite standard solution

See 5.1.6.1.

The mass concentration of this solution is:

$$\rho(SO_3) = 100 \text{ mg/l}$$

– Into a graduated flask of nominal capacity 100 ml, pipette approximately 80 ml of water (4.1), 1 ml of sodium hydroxide solution (4.1.10), 0,1 ml of formaldehyde solution (5.1.2), 10 ml of the stock solution, prepared as described in 5.1.5, and dilute to volume with water (4.1).

Prepare the solution freshly before use.

Prepare further standard solutions by appropriate dilutions of this standard solution.

5.1.7 Sulfite calibration solutions

Depending on the anion concentration expected, use the standard solution (5.1.6.2) to prepare 5 to 10 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 of sulfite.

– Into a series of graduated flasks of nominal capacity 100 ml, transfer approximately 80 ml of water (4.1), 1 ml of sodium hydroxide solution (4.1.10), 0,1 ml of formaldehyde solution (5.1.2). Pipette 1 ml, 2 ml, 3 ml, 4 ml, 5 ml, 6 ml, 7 ml, 8 ml, 9 ml and 10 ml respectively of the standard solution (5.1.6.2), dilute to volume with water (4.1).

The concentrations of sulfite in the 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.

5.1.8 Blank solution

Prepare the blank solution in accordance with 4.1.20.

5.2 Apparatus

In addition to the apparatus mentioned in 4.2.1 to 4.2.3 (including the quality requirements of the separator system), a cation exchanger in Ag-form (cartridge) shall be used.

5.3 Interferences

See 4.3.

The presence of bromide, chloride, nitrate, nitrite, phosphate and sulfate can in particular cause interference with the determination of sulfite (table 3), whose retention strongly depends on the selectivity of the separator column used. Remove halides with the aid of special exchangers (5.2, 5.4.2).

The following cross-sensitivities (see table 3) need to be taken into account:

Table 3 — Cross-sensitivity of the anion

Ratio of mass concentrations of solute to interfering ion		Mode of detection
SO_3^{2-}/SO_4^{2-}	1:1000	CD with suppression
SO_3^{2-}/PO_4^{3-}	1: 100	CD with suppression
SO_3^{2-}/PO_4^{3-}	1: 50	CD without suppression
SO_3^{2-}/F^-	1: 10	CD without suppression
SO_3^{2-}/Cl^-	1: 50 *)	CD without suppression
*) If eluents of 5.1.4.2.2 or 5.1.4.3 are used, a sample pretreatment (according to 5.4.2) is normally required.		

When applying the procedure described in 5.4, calcium ions present in high concentrations can cause precipitation of calcium sulfite and consequently lead to erroneously low results.

5.4 Sampling and sample pretreatment

5.4.1 General requirements

In addition to the procedure described in 4.4:

- Use only glass containers for sampling.
- After sample collection adjust the pH of the sample with sodium hydroxide solution (4.1.10) to approximately pH 10 (e.g. 1 ml of sodium hydroxide to 1 l of sample) and add formaldehyde solution (5.1.2) in the ratio 1 part formaldehyde solution + 1 000 parts sample.
- Treat blank solution (5.1.8) and calibration solutions (5.1.7) in the same manner.

5.4.2 Sample pretreatment in order to avoid interference with chloride

Depending on the type of separating column, eluent and detection mode, chloride can interfere with the determination of sulfite (5.3, table 3). Adjust a ratio of ≤ 50 parts of chloride to 1 part of sulfite to avoid separation problems with the elution of sulfite near to the chloride. Proceed as follows:

– Dilute the sample, if necessary, and run it through a strongly acid cation exchanger in the Ag-form (cartridge[15]), 5.2) to remove dissolved chloride from the eluate.

– Run the filtrate through a cation exchanger in the H-form (cartridge[15]), 5.2.3) to remove dissolved silver ions from the eluate.

– Chromatograph the treated sample as described in 5.5.

– Treat the blank solution (5.1.8) and calibration solutions (5.1.7) in the same manner.

5.5 Procedure

Analyse as described in 4.5 and 4.5.2.

5.5.1 Calibration

Perform the calibration according to 4.5.1 (see ISO 8466-1). Check the validity of the calibration function in accordance with 4.5.2.1.

5.6 Calculation

Calculate as described in 4.6.

5.7 Expression of results

Report the results to a maximum of two significant figures.

EXAMPLE

Sulfite (SO_3^{2-}) 13 mg/l

5.8 Test report

See 4.8, with the results presented according to 5.7.

6 Determination of chromate

Follow the instructions given in clause 6 to make the working ranges given in table 1 feasible.

15) Before use rinse the cartridge with water (4.1).

6.1 Reagents

In addition to the reagents listed in 4.1, the following reagents are used.

6.1.1 Pyridine-2,6-dicarboxylic acid, $C_7H_5NO_4$

6.1.2 Disodium hydrogenphosphate, Na_2HPO_4

6.1.3 Sodium acetate, $C_2H_3NaO_2$

6.1.4 Acetone, C_3H_6O

6.1.5 Ammonium sulfate, $H_8N_2O_4S$

6.1.6 Ammonia solution, $w(NH_3)$ = 25 % (aqueous solution)

6.1.7 Potassium chromate, K_2CrO_4

6.1.8 Lithium hydroxide, LiOH

6.1.9 Eluents

The general remarks of 4.1.16.1 on suitability and composition of mobile phases remain valid for the determination of chromate. Obtain the exact composition of the eluents from the column manufacturer's instructions.

In 6.1.9.1 and 6.1.9.2 two examples of eluents are described.

6.1.9.1 Eluent I

– Place 0,836 g of pyridine-2,6-dicarboxylic acid (6.1.1), 0,71 g of disodium hydrogenphosphate (6.1.2), 3,75 g of sodium iodide (4.1.14), 10,25 g of sodium acetate (6.1.3), 0,17 g of lithium hydroxide (6.1.8), into a graduated flask of nominal capacity 5 000 ml, dissolve in water (4.1), add 250 ml of acetone (6.1.4), and dilute to volume with water (4.1).

The solution contains 0,001 mol/l of pyridine-2,6-dicarboxylic acid, 0,001 mol/l of disodium hydrogenphosphate, 0,005 mol/l of sodium iodide, 0,025 mol/l of sodium acetate, and 0,0014 mol/l of lithium hydroxide and approximately 5 % of acetone. Renew the eluent every 2 to 3 days (4.1.16).

6.1.9.2 Eluent II

– Place 165 g of ammonium sulfate (6.1.5) and 38 ml of ammonia solution (6.1.6) into a graduated flask of nominal capacity 5 000 ml, and dilute to volume with water (4.1).

The solution contains 0,25 mol/l of ammonium sulfate and 0,1 mol/l of ammonium hydroxide. Renew the eluent every 2 to 3 days (4.1.16).

6.1.10 Chromate standard stock solution

Prepare the standard stock solution of concentration 1 000 mg/l (CrO_4) as follows:

– Dry approximately 1,8 g of potassium chromate (6.1.7) for 3 h at 105 °C. Cool in a desiccator.
– Place 1,674 g of potassium chromate (6.1.7), dissolved in water (4.1), into a graduated flask of nominal capacity 1 000 ml. Make alkaline with 1 ml of sodium hydroxide solution (4.1.10) and dilute to volume with water (4.1).

6.1.11 Chromate standard solution

The mass concentration of this solution is:

$$\rho\ (CrO_4) = 10\ mg/l$$

– Pipette 1 ml of the stock solution (6.1.10) into a graduated flask of nominal capacity 100 ml, make alkaline with 1 ml of sodium hydroxide solution (4.1.10) and dilute to volume with water (4.1).

Prepare the solution on the day of measurement. Prepare further standard solutions as required from this standard chromate solution.

6.1.12 Chromate calibration solutions

Always use the same vessels for the same concentration ranges in order to avoid the danger of cross-contamination.

– Depending on the anion concentration to be expected, use the standard solution (6.1.11) to prepare 5 to 10 calibration solutions covering the expected working range as evenly as possible.

Proceed, for example, for the working range from 0,1 mg/l to 1 mg/l of chromate, as follows.

– Into a series of 10 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 standard solution respectively (6.1.11), make alkaline with 1 ml of sodium hydroxide solution (4.1.10), and dilute to volume with water (4.1).

The chromate concentrations in the calibration solutions are 0,1 mg/l, 0,2 mg/l, 0,3 mg/l, 0,4 mg/l, 0,5 mg/l, 0,6 mg/l, 0,7 mg/l, 0,8 mg/l, 0,9 mg/l and 1,0 mg/l respectively.

Prepare the calibration solutions on the day of use.

6.1.13 Blank solution

Prepare the blank solution in accordance with 4.1.20.

6.2 Apparatus

Use the apparatus mentioned in 4.2.1 to 4.2.3 (including the quality requirements of the separation system). For detection use only a UV/VIS detector.

6.3 Interferences

For the determination of chromate, interferences will not normally occur when a UV detector is used.

6.4 Sampling and sample pretreatment

In contrast to the procedure described in 4.4, proceed as follows:

– Immediately after sample collection, adjust the pH of the sample to 9 with sodium hydroxide solution (4.1.10).
– Treat the blank solution (6.1.13) and calibration solutions (6.1.12) in the same manner.

6.5 Procedure

Analyse in accordance with 4.5 and 4.5.2.

6.5.1 Calibration

Perform the calibration in accordance with 4.5.1. Check the validity of the calibration function according to 4.5.2.2.

6.6 Calculation

Calculate in accordance with 4.6.

6.7 Expression of results

Report the results to a maximum of two significant figures.

EXAMPLE
Chromate (CrO_4^{2-}) $1,7 \times 10^{-1}$ mg/l

The results can also be expressed as follows. To convert the results multiply:

(CrO_4^{2-}) by 0,4483 for (Cr)
(Cr) by 2,231 for (CrO_4^{2-}).

6.8 Test report

See 4.8, with the results presented according to 6.7.

7 Precision

Details of an interlaboratory trial on the precision of the method are summarized in annex A. The values derived from this interlaboratory test may not be applicable to concentration ranges and matrices other than those given.

Annex A
(informative)

Interlaboratory trials

An interlaboratory trial was organized in Germany in 1991, with laboratories from France and Germany participating. A variety of instruments and other analytical conditions (see table A.1) were used which conformed with the quality parameters specified in these methods.

The statistical results are presented in tables A.2 to A.6.

The coefficients of variation of the procedure V_{xo} (obtained from determined calibration functions) are listed in table A.7. These data were also obtained from laboratories participating in the interlaboratory trial in Germany in 1991 from calibration experiments analogous to those described in 4.5.1.

Table A.1 — Description of sample matrix and sample pretreatment

Sample matrix	Description of sample							
	COD	Cl	SO_4	NO_3	NH_4-N	P_{total}	Ni	Cr_{total}
	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l
Drinking water	< 5	40	50	5	—**	0,2	< 0,1	—**
Synthetic drinking water	< 5	60	60	6	< 0,1	—**	< 0,1	—**
Treated domestic sewage	33	33	130	0,8	9	0,8	< 0,1	—**
Treated industrial sewage	10	23	43	0,8	—**	< 0,1	2,0	0,12

NOTE Membrane filtration of pore size 0,45 µm) and adjustment to pH 9 of samples were carried out before mailing.
* COD: Chemical oxygen demand.
** — : Not determined.

Table A.2 — Statistical data for iodide (I)

Sample	I	n	KA_1	$\bar{x}$	s_R	CV_R	s_r	CV_r
			%	mg/l	mg/l	%	mg/l	%
Drinking water, synthetic	19	69	0	0,248	0,019	7,51	0,012	4,89
Sewage, industrial	19	67	0	0,491	0,026	5,23	0,016	3,14
Sewage, domestic	19	67	2,9	0,751	0,056	7,45	0,030	3,95

I is the number of participating laboratories;
n is the number of analytical values per level;
KA_1 is the percentage of outlying values from the replicates in all laboratories;
$\bar{x}$ is the total mean;
s_R is the standard deviation of reproducibility;
CV_R is the coefficient of variation of the reproducibility;
s_r is the standard deviation of the repeatability;
CV_r is the coefficient of variation of the repeatability.

NOTE All samples spiked with I^-, SCN^-, $S_2O_3^{2-}$ mixed standard solution.

Table A.3 — Statistical data for thiocyanate (SCN)

Sample	l	n	KA_1 %	$\bar{x}$ mg/l	s_R mg/l	CV_R %	s_r mg/l	CV_r %
Drinking water	23	73	12	2,46	0,093	3,76	0,065	2,65
Sewage, industrial	21	69	12,7	4,88	0,142	2,91	0,085	1,75
Sewage, domestic	23	81	2,4	7,19	0,400	5,56	0,143	1,99

NOTE 1 Definition of symbols see table A.2.
NOTE 2 All samples spiked with I^-, SCN^-, $S_2O_3^{2-}$ mixed standard solution.

Table A.4 — Statistical data for thiosulfate (S_2O_3)

Sample	l	n	KA_1 %	$\bar{x}$ mg/l	s_R mg/l	CV_R %	s_r mg/l	CV_r %
Drinking water	22	75	7,4	1,96	0,132	6,72	0,076	3,89
Sewage, industrial	21	69	12,6	3,94	0,111	2,81	0,064	1,63
Sewage, domestic	23	66	20,5	5,88	0,132	2,25	0,064	1,09

NOTE 1 Definition of symbols see table A.2.
NOTE 2 All samples spiked with I^-, SCN^-, $S_2O_3^{2-}$ standard solution.

Table A.5 — Statistical data for sulfite (SO_3)

Sample	l	n	KA_1 %	$\bar{x}$ mg/l	s_R mg/l	CV_R %	s_r mg/l	CV_r %
Drinking water, synthetic	13	48	0	1,28	0,144	11,3	0,044	3,44
Sewage, industrial	13	45	8,2	2,47	0,164	6,6	0,082	3,32
Sewage, domestic	11	38	9,5	3,22	0,520	16,1	0,086	4,54

NOTE 1 Definition of symbols see table A.2.
NOTE 2 All samples spiked with SO_3^{2-} standard solution.

Table A.6 — Statistical data for chromate (CrO_4)

Sample	l	n	KA_1 %	$\bar{x}$ mg/l	s_R mg/l	CV_R %	s_r mg/l	CV_r %
Drinking water	10	35	5,4	0,122	0,011	8,66	0,008	6,29
Sewage, industrial	10	33	10,8	0,370	0,012	3,31	0,010	2,76
Sewage, domestic	10	36	0	0,239	0,021	8,95	0,008	3,22

NOTE 1 Definition of symbols see table A.2.
NOTE 2 All samples spiked with CrO_4^{2-} standard solution.

Table A.7 — Estimation of performance characteristics indicated by coefficients of variation of the procedure (V_{XO})

Anion	V_{XO} %	Examined working ranges mg/l
Chromate (CrO_4)	0,8 to 2,7	0,05 to 0,50
Iodide (I)	0,5 to 3,6	0,1 to 1,0
Sulfite (SO_3)	0,7 to 3,4	1,0 to 10
Thiocyanate (SCN)	0,4 to 2,8	1,0 to 10
Thiosulfate (S_2O_3)	0,4 to 3,6	1,0 to 10

Annex B
(informative)

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