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Water quality — Determination of dissolved Li^+, Na^+, NH_4^+, K^+, Mn^{2+}, Ca^{2+}, Mg^{2+}, Sr^{2+} and Ba^{2+} using ion chromatography — Method for water and waste water

Qualité de l'eau — Dosage, par chromatographie ionique, des ions Li^+, Na^+, NH_4^+, K^+, Mn^{2+}, Ca^{2+}, Mg^{2+}, Sr^{2+} et Ba^{2+} dissous — Méthode applicable pour l'eau et les eaux résiduaires

Reference number
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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 14911 was prepared by Technical Committee TC 147, *Water quality*, Subcommittee SC 2, *Physical, chemical, biochemical methods.*

Annexes A and B of this International Standard are for information only.

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Introduction

The essential minimum requirements of an ion chromatographic system applied within the scope of this International Standard are given in clause 5.

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

Further information on the analytical technique is given in the normative references (see clause 2) and the bibliography.

Water quality — Determination of dissolved Li^+, Na^+, NH_4^+, K^+, Mn^{2+}, Ca^{2+}, Mg^{2+}, Sr^{2+} and Ba^{2+} using ion chromatography — Method for water and waste water

1 Scope

This International Standard specifies a method for the determination of the dissolved cations Li^+, Na^+, NH_4^+, K^+, Mn^{2+}, Ca^{2+}, Mg^{2+}, Sr^{2+} and Ba^{2+} in water (e.g. drinking water, surface water, waste water).

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

The applicability of the method for waste water samples should be proved in each case.

Table 1 — Working ranges of the analytical method

Cation	Typical working range with 10 µl loop mg/l[1)]
Lithium	0,01 to 1
Sodium	0,1 to 10
Ammonium	0,1 to 10
Potassium	0,1 to 10
Manganese	0,5 to 50
Calcium	0,5 to 50
Magnesium	0,5 to 50
Strontium	0,5 to 50
Barium	1 to 100

1) The working range is limited by the ion-exchange capacity of the separator column. If necessary, the sample shall be diluted to meet the working range, or use a 100 µl loop for lower working ranges.

2 Normative references

The following standards contain provisions which, through reference in this text, constitute provisions of this International Standard. 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 6058:1984, *Water quality — Determination of calcium content — EDTA titrimetric method.*

ISO 6059:1984, *Water quality — Determination of the sum of calcium and magnesium — EDTA titrimetric method*

ISO 6333:1986, *Water quality — Determination of manganese — Formaldoxime spectrometric method.*

ISO 7980:1986, *Water quality — Determination of calcium and magnesium — Atomic absorption spectrometric method.*

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 8466-2:1993, *Water quality — Calibration and evaluation of analytical methods and estimation of performance characteristics — Part 2: Calibration strategy for non-linear second order calibration functions.*

3 Interferences

3.1 Organics such as amino acids and aliphatic amines can interfere with the determination of inorganic cations.

3.2 If a strong complexing agent such as pyridine-2,6-dicarboxylic acid (PDA) is not present in the mobile phase, and if the suppressor technique is not used, cross interferences from other cations like Zn^{2+}, Ni^{2+}, Cd^{2+} etc. can occur.

3.3 Cross-sensitivities with other cations, e.g. manganese, are dependent on the selectivity of the separator column used. If the quality requirements in clause 8 are not achieved, the sample shall be diluted.

3.4 Cross-sensitivities in the determination of NH_4^+ and Na^+ can occur when there are large differences in concentration.

3.5 Solid material and organic compounds (such as mineral oils, detergents and humic acids) shorten the lifetime of the separator column. They are therefore eliminated from the sample (9.3).

4 Principle

Liquid chromatographic separation of Li^+, Na^+, NH_4^+, K^+, Mn^{2+}, Ca^{2+}, Mg^{2+}, Sr^{2+} and Ba^{2+} by means of a separator column. A low-capacity cation exchanger is used as the stationary phase, and usually, aqueous solutions of mono- and dibasic acids as mobile phases (eluent, see 6.16).

These cations are detected by conductivity. It is essential that the eluents have a sufficiently low conductivity. For this reason, a conductivity detector (CD) is often combined with a suppressor device (e.g. an anion exchanger) which will reduce the conductivity of the eluent and transform the separated cations into their corresponding bases.

In the conductivity detection without chemical suppression, the difference between the ion equivalent conductivities is measured directly after the column. This difference should be as high as possible and the detector cell temperature should be stabilized within $\pm 0{,}1$ °C.

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

5 Essential minimum requirements

The essential minimum requirements of an ion chromatographic system applied within the scope of this International Standard are the following:

a) Resolution power (R) of the column:	For the cation to be determined it is essential that the peak resolution does not fall below R = 1,3 (see clause 8, figure 3).
b) Method of detection:	Measurement of the electrical conductivity with or without suppressor device.
c) Applicability of the method:	Working ranges according to table 1.
d) Calibration (10.2):	Calibration and determination of the linear (see ISO 8466-1) or quadratic (see ISO 8466-2) working range. Use of the method of standard addition to special cases of application (see 10.3).
e) Guaranteeing the analytical quality (10.3.2):	Validity check of the calibration function. Replicate determinations, if necessary.

6 Reagents

Use only reagents of recognized analytical grade. 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.

6.1 DL-2,3-Diaminopropionic acid monohydrochloride (DAP), $C_3H_8N_2O_2 \cdot HCl$.

6.2 Hydrochloric acid solution, c(HCl) = 7,7 mol/l.

6.3 Methanesulfonic acid, CH_4O_3S (≥ 99%).

6.4 Pyridine 2,6-dicarboxylic acid (PDA), $C_7H_5NO_4$.

6.5 Tartaric acid, $C_4H_6O_6$.

6.6 Nitric acid solution, $c(HNO_3)$ = 1 mol/l.

6.7 Lithium nitrate, $LiNO_3$.

6.8 Sodium nitrate, $NaNO_3$.

6.9 Ammonium chloride, NH_4Cl.

6.10 Potassium nitrate, KNO_3.

6.11 Manganese nitrate tetrahydrate, $Mn(NO_3)_2 \cdot 4H_2O$.

6.12 Calcium nitrate tetrahydrate, $Ca(NO_3)_2 \cdot 4H_2O$.

6.13 Magnesium nitrate hexahydrate, $Mg(NO_3)_2 \cdot 6H_2O$.

6.14 Strontium nitrate, $Sr(NO_3)_2$.

6.15 Barium nitrate, $Ba(NO_3)_2$.

6.16 Eluents, their choice depending on the type of separator column and detector.

Follow the column manufacturer´s instructions for the exact composition of the eluent. The eluent compositions described in 6.16.1.1, 6.16.1.2, 6.16.2.1.1 and 6.16.2.2 are examples only.

A selection of reagents for preparing common eluents is presented in 6.1 to 6.6.

Degas all eluents or prepare eluents using degassed water. Avoid any renewed gas pick-up during operation (e.g. by helium sparging). Store the eluents in the dark and renew as required.

6.16.1 Examples of eluents for ion chromatography using the suppressor technique

For the application of the suppressor technique, solutions containing strong acids like hydrochloric acid or methanesulfonic acid or mixtures of these acids with DAP (6.1) can be used. Eluent concentrates are not recommended, but can be used.

6.16.1.1 Hydrochloric acid / DAP eluent

The following eluent is applicable for the determination of Li^+, Na^+, NH_4^+, K^+, Mn^{2+}, Ca^{2+}, Mg^{2+}, Sr^{2+} and Ba^{2+}:

Place 5,2 ml of a hydrochloric acid solution (6.2) and 0,562 g ± 0,006 g of DAP (6.1) into a 1000 ml volumetric flask and dilute to volume with degassed water.

The solution contains 0,04 mol/l of hydrochloric acid and 0,004 mol/l DAP (6.1). Store the solution at 4 °C to 6 °C, renew it every 7 d.

6.16.1.2 Methanesulfonic acid eluent

The following eluent is applicable for the determination of Li^+, Na^+, NH_4^+, K^+, Mn^{2+}, Ca^{2+}, Mg^{2+}, Sr^{2+} and Ba^{2+}:

Place 1,3 ml of methanesulfonic acid-solution (6.3) into a 1000 ml volumetric flask and dilute to volume with degassed water.

The solution contains 0,02 mol/l of methanesulfonic acid. Renew the eluent every 3 d.

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

For ion chromatography techniques without suppressor devices, acids like nitric, tartaric, oxalic etc. are used. The solutions can contain various additions, e.g. alcohols. The concentration of the acids is usually in the range of 0,001 mol/l to 0,01 mol/l. Concentrate and eluent solutions are prepared as described in 6.16.

6.16.2.1 Tartaric acid/PDA concentrate

The eluent concentrate has proved to be successful for the eluent preparation (6.16.2.1.1):

Place 1,671 g ± 0,017 g of PDA (6.4) in a beaker of capacity 1000 ml, add approximately 500 ml of water (clause 6). Stir and dissolve by heating (60 °C to 80 °C). After cooling add 6,003 g ± 0,060 g tartaric acid (6.5) and transfer the cool solution into a 1000 ml volumetric flask and dilute to volume with water.

The solution contains 0,01 mol/l PDA and 0,04 mol/l tartaric acid and is stable for one month if stored at 4 °C to 6 °C.

6.16.2.1.1 Tartaric acid/PDA eluent

For the determination of Li^+, Na^+, NH_4^+, K^+, Mn^{2+}, Ca^{2+}, Mg^{2+}, Sr^{2+} and Ba^{2+}, the following eluent has proved to be successful:

Place 100 ml of the concentrate (6.16.2.1) into a 1000 ml volumetric flask and dilute to volume with water (clause 6).

The solution contains 0,001 mol/l PDA and 0,004 mol/l tartaric acid. The eluent pH is 2,8. Renew the eluent every 3 d.

6.16.2.2 Nitric acid eluent

For the determination of Li^+, Na^+, NH_4^+, K^+, Mn^{2+}, Ca^{2+}, Mg^{2+}, Sr^{2+} and Ba^{2+}, the following eluent has proved to be successful:

Place 500 ml of water (clause 6) into a 1000 ml volumetric flask, add 20 ml of the nitric acid solution (6.6) and dilute to volume with water.

The solution contains 0,02 mol/l nitric acid. Renew the eluent every 3 d.

6.17 Stock solutions

Prepare stock solutions of concentration $\rho = 1000$ mg/l for each of the cations Li^+, Na^+, NH_4^+, K^+, Mn^{2+}, Ca^{2+}, Mg^{2+}, Sr^{2+} and Ba^{2+}:

Dissolve the appropriate mass of each of the substances, prepared as stated in table 2, in approximately 800 ml of water (clause 6, degassed with nitrogen or helium), in 1000 ml volumetric flasks of polyethylene, add 1 ml nitric acid solution (6.6). Dilute to volume with water. The solutions are stable for six months if stored at 4 °C to 6 °C in polyethylene bottles.

Table 2 — Mass of portion and suggestions how to store stock solutions

Cation	Salt[1)]	Concentration derived from substance-portion g/l	Pretreatment	Storage at 4 °C to 6 °C in polyethylene bottles
Lithium	$LiNO_3$	9,933 7 ± 0,099	Dry at 105°C ± 5 °C, 2 h	in 0,001 mol/l HNO_3[2)]
Sodium	$NaNO_3$	3,697 9 ± 0,037	Dry at 105°C ± 5 °C	in water
Ammonium	NH_4Cl	2,965 5 ± 0,030	Dry at 105°C± 5 °C	in water
Potassium	KNO_3	2,586 0 ± 0,026	Dry at 105°C ± 5 °C	in water
Manganese	$Mn(NO_3)_2 \cdot 4\ H_2O$	4,569 0 ± 0,046[3)]	Dry in a desiccator	in 0,001 mol/l HNO_3[2)]
Calcium	$Ca(NO_3)_2 \cdot 4\ H_2O$	5,892 0 ± 0,059[3)]	Dry in a desiccator	in 0,001 mol/l HNO_3[2)]
Magnesium	$Mg(NO_3)_2 \cdot 6\ H_2O$	10,549 7 ± 0,105[3)]	Dry in a desiccator	in 0,001 mol/l HNO_3[2)]
Strontium	$Sr(NO_3)_2$	2,415 3 ± 0,024	Dry at 105°C ± 5 °C	in 0,001 mol/l HNO_3[2)]
Barium	$Ba(NO_3)_2$	1,903 1 ± 0,019	Dry at 105°C ± 5 °C	in 0,001 mol/l HNO_3[2)]

1) Alternatively, use commercially available solutions of the respective cation and nitric acid concentrations.

2) Check the content of analyte before use.

3) Titre adjustment is neccessary prior to use (for Mn: in accordance with ISO 6333; for Ca/Mg: in accordance with ISO 7980 or ISO 6058/ISO 6059).

6.18 Mixed standard solutions

Depending upon the concentrations expected, prepare standard solutions of different cation composition and concentration from the stock solutions (6.17). The risk of changes in concentration caused by interaction with the vessel material increases with decreasing cation concentration. The lower the sodium and potassium concentration in the standard solution, the higher the probability of a change in concentration due to an interaction with the vessel material. Store the standard solutions in polyethylene vessels.

6.18.1 Mixed standard solution of Li^+, Na^+, NH_4^+, K^+, Mn^{2+}, Ca^{2+}, Mg^{2+}, Sr^{2+} and Ba^{2+}

The mass concentrations of the solutions are given in table 3. If only some of the cations listed in tables 3 and 4 have to be determined, the following steps are applicable for those cations only.

Place in a 100 ml polyethylene volumetric flask approximately 50 ml of water (clause 6), add 1 ml nitric acid solution (6.6), and pipette the volume of each of the substances as stated in table 3, and fill up to volume with water (clause 6). Store the solution in a polyethylene vessel. If stored at 2 °C to 6 °C, the solution is stable for one week.

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

Cation	Stock solution ml	Cation concentration mg/l
Li^+	0,5	5
Na^+	1,0	10
NH_4^+	1,0	10
K^+	2,0	20
Mn^{2+}	2,0	20
Ca^{2+}	2,0	20
Mg^{2+}	2,0	20
Sr^{2+}	5,0	50
Ba^{2+}	10,0	100

Other mixed standard solutions can be made by respective dilutions of the mixed standard solution.

6.19 Cation calibration solutions

Depending on the cation concentration expected, use the stock solutions or the mixed standard solutions (6.17 or 6.18.1) to prepare 5 to 10 calibration solutions distributed over the expected working range as equally as possible.

For example, proceed as follows for the ranges:

a) 0,05 mg/l to 0,5 mg/l Li^+

b) 0,1 mg/l to 1,0 mg/l Na^+, NH_4^+

c) 0,2 mg/l to 2,0 mg/l K^+, Mn^{2+}, Ca^{2+}, Mg^{2+}

d) 0,5 mg/l to 5,0 mg/l Sr^{2+}

e) 1,0 mg/l to 10,0 mg/l Ba^{2+}

Pipette into a series of 100 ml polyethylene volumetric flasks a volume of 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 (6.18.1), add 0,1 ml nitric acid solution (6.6) and dilute to volume with water (clause 6).

The concentrations of the calibration solutions are listed in table 4. Prepare the calibration solutions on the day of use.

Table 4 — Concentrations of the calibration solutions

Cation	Concentrations of the calibration solutions mg/l
Li^+	0,05; 0,1; 0,15; 0,2; 0,25; 0,3; 0,35; 0,4; 0,45; 0,50
Na^+	0,1; 0,2; 0,3; 0,4; 0,5; 0,6; 0,7; 0,8; 0,9; 1,0
NH_4^+	0,1; 0,2; 0,3; 0,4; 0,5; 0,6; 0,7; 0,8; 0,9; 1,0
K^+	0,2; 0,4; 0,6; 0,8; 1,0; 1,2; 1,4; 1,6; 1,8; 2,0
Mn^{2+}	0,2; 0,4; 0,6; 0,8; 1,0; 1,2; 1,4; 1,6; 1,8; 2,0
Ca^{2+}	0,2; 0,4; 0,6; 0,8; 1,0; 1,2; 1,4; 1,6; 1,8; 2,0
Mg^{2+}	0,2; 0,4; 0,6; 0,8; 1,0; 1,2; 1,4; 1,6; 1,8; 2,0
Sr^{2+}	0,5; 1,0; 1,5; 2,0; 2,5; 3,0; 3,5; 4,0; 4,5; 5,0
Ba^{2+}	1,0; 2,0; 3,0; 4,0; 5,0; 6,0; 7,0; 8,0; 9,0; 10,0

6.20 Blank solutions

Fill a 100 ml volumetric flask up to volume with water (clause 6) and add 0,1 ml nitric acid solution (6.6).

7 Apparatus

Usual laboratory apparatus, and, in particular

7.1 Ion chromatographic system, complying with the quality requirements of clause 8. In general, it shall consist of the following components (see figure 1):

a) eluent reservoir;

b) pump, suitable for HPLC;

c) sample injection system incorporating a sample loop (e.g. sample loop of volume 10 µl);

d) precolumn (see 10.3.1) e.g. containing the same resin material as the analytical seperator column or packed with a macroporous polymer;

e) separator column with the specified separating performance (see clause 8);

f) conductivity detector (with or without a suppressor device assembly);

g) recording device;

h) cartridges or columns with non-polar phases to be used for sample preparation (e.g. polyvinylpyrrolidone).

8 Quality requirements for the separator column

Separation conditions shall be such that possible interfering cations will not interfere with the cations of interest at a concentration of 0,1 mg/l Li^+, 1 mg/l Na^+ or NH_4^+, 2 mg/l K^+, Mn^{2+}, Ca^{2+} or Mg^{2+}, 5 mg/l Sr^{2+} and 10 mg/l Ba^{2+} (see figure 2).

Regarding chromatograms of samples and standard solutions with higher concentrations, peak resolution R shall not fall below R = 1,3 [see equation (1) and figure 3] for any pair of peaks.

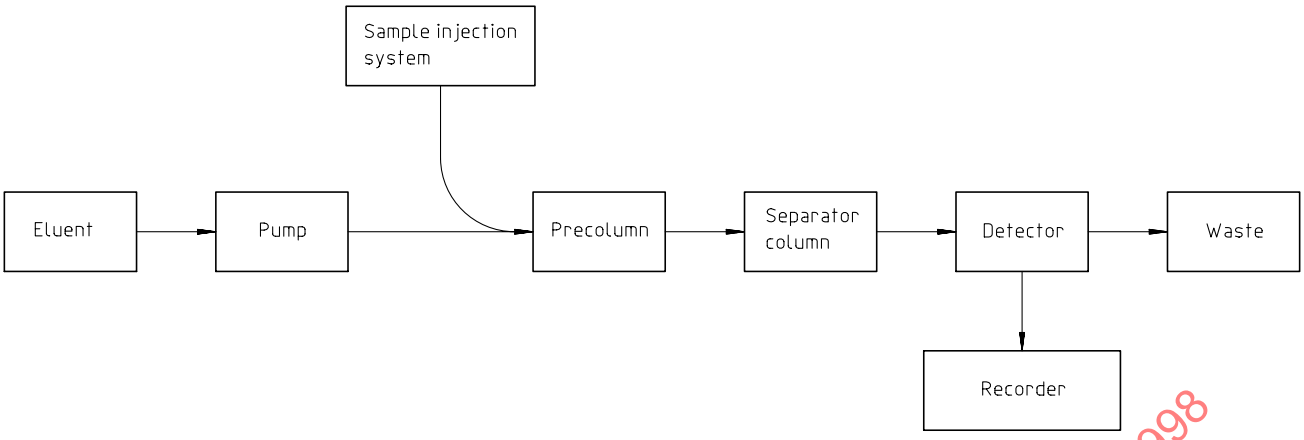
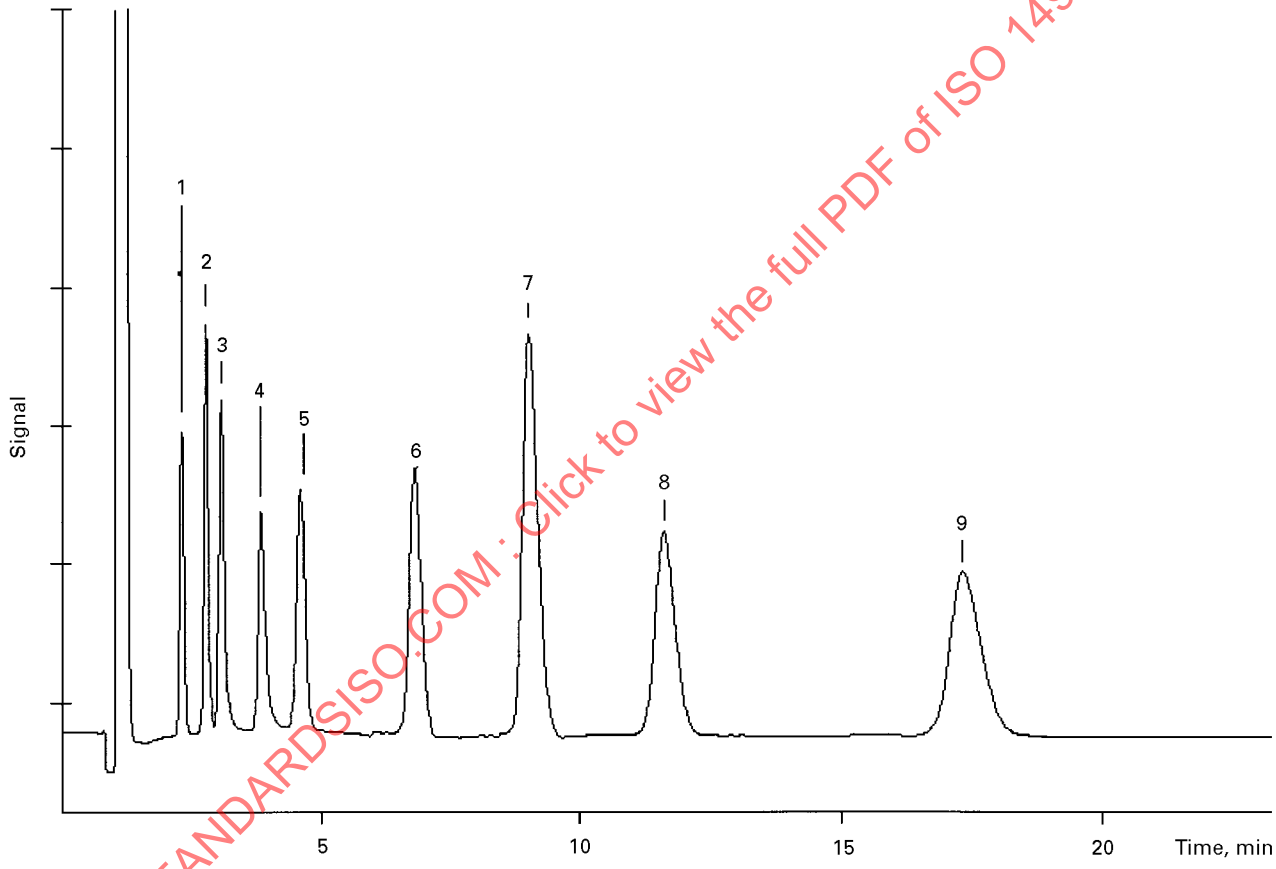


Figure 1 — Schematic representation of an ion chromatography system



Key

1 Lithium
2 Sodium
3 Ammonium
4 Potassium
5 Manganese
6 Calcium
7 Magnesium
8 Strontium
9 Barium

NOTE Elution sequences and retention times (t_R) can vary, depending on the type of column and the eluent composition

Figure 2 — Example of a chromatogram of a column conforming to this International Standard

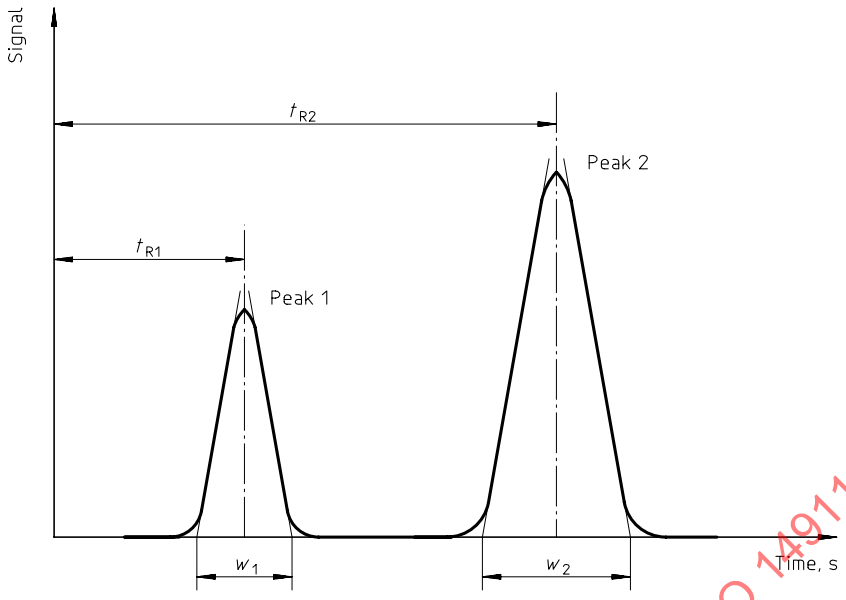


Figure 3 — Graphical representation of the parameters to calculate the peak resolution R

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

where

$R_{2,1}$ is the resolution for the peak pair 2,1;

t_{R1} is the retention time, in seconds, of the first peak;

t_{R2} is the retention time, in seconds, of the second peak;

w_1[1)] is the peak width, in seconds, on the time axis of the first peak;

w_2[1)] is the peak width, in seconds, on the time axis of the second peak.

9 Sampling and sample pretreatment

9.1 It is important to ensure that the laboratory receives a sample which is truly representative and has not been damaged or changed during transport or storage. Sampling procedures shall be in accordance with ISO 5667-1, ISO 5667-2 and ISO 5667-3.

9.2 Use only clean polyethylene (never glass) vessels for sampling.

9.3 After sample collection, filter it through a membrane filter (of pore size 0,45 µm) and adjust the pH of the sample to a value of 3 ± 0,5 with nitric acid solution (6.6), to prevent precipitation or conversion of cations by bacterial growth.

NOTE If the pH falls below this level then the concentration of nitrate ions can interfere with the analysis.

1) w_1, w_2 are the base widths of the isosceles triangles constructed representing four times the standard deviation of the Gaussian peak.

9.4 Carry out the analyses as soon as possible after sampling. If an immediate analysis is not feasible, stabilize the membrane filtered sample by cooling it (2 °C to 6 °C), provided the results will not be impaired for determinants of interest.

9.5 If ammonia is to be determined, store the sample in the dark (2 °C to 6 °C) and analyse it within 24 h.

9.6 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).

9.7 Waters strongly contaminated with organics 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. polyvinylpyrrolidone phase; 7.1 h)] prior to injection (10.3).

9.8 Treat calibration solution (6.19) and blank solution (6.20) in the same manner as the sample solutions.

10 Procedure

10.1 General

Set up the ion chromatograph (7.1) 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 10.2. Measure samples and blank solutions (6.20) as described in 10.3.

10.2 Calibration

10.2.1 General

Inject the calibration solutions. Identify the peaks for particular cations by comparing the retention times with those of the standard solutions (see 6.19). 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 cation.

When the analytical system is first evaluated, and at intervals afterwards, establish a calibration function (see ISO 8466-1 or ISO 8466-2) for the measurement as follows.

a) Prepare calibration solutions as described in 6.19;

b) analyse the calibration solutions chromatographically;

c) use the data obtained to calculate the regression line according to 10.2.2 or 10.2.3;

d) subsequently, check the continuing validity of the established calibration function [see a) above].

10.2.2 Calibration using first order calibration function

Reject if it is not linear (for linearity criteria, refer to ISO 8466-1) or calculate the calibration function using a second order function (10.2.3).

The following equation (first order calibration function) applies for the ion i to be determined:

$$Y_i = b_i \cdot \rho_i + a_{0,i} \qquad (2)$$

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;

$a_{o,i}$ is the ordinate intercept of the calibration function (calculated blank), e.g. mm, µV · s.

10.2.3 Calibration using second order calibration function

The following equation (second order calibration function) applies for the ion i to be determined:

$$Y_i = c_i \cdot \rho_i^2 + b_i \cdot \rho_i + a_{o,i} \quad (3)$$

where

c_i is the second order coefficient of the calibration function, of e.g. mm · l²/mg²; µV · s · l²/mg²;

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

For an explanation of Y_i, ρ_i, $a_{o,i}$ see equation (2).

10.3 Measurement of samples using the standard calibration procedure

10.3.1 General

After establishing the calibration function, inject the pretreated sample (clause 9) into the chromatograph and measure the peaks as above (see clause 10).

In general, the use of a precolumn is strongly recommended, especially for the injection of waters strongly contaminated with organics (see 9.7). It serves to protect the analytical separator column. In general, two different types of precolumns can be used: those containing the same resin material as the analytical separator column and those packed with a macroporous polymer [see 7.1 d)].

If the ion concentration of the sample to be analysed exceeds the calibration range, dilute the sample and analyse it. Sometimes it is 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 time of the spiked sample with those of the original sample).

Measure the blank solution (see 6.20) in the same manner.

10.3.2 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 part of the working range. This should take place after the set-up procedure (see 10.1) and after each sample series at least, but in any case after 20 measurements.

Calculate the mass concentrations of the analysed calibration solutions using the inverse calibration function (see clause 11, equation (4) or (5). 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 10.2).

11 Calculation

11.1 General

Estimate the mass concentration (ρ_i) in milligrams per litre, of the cation in the solution using the peak areas or peak heights using the first order (11.2) or second order calibration function (11.3).

11.2 Calculation using the first order calibration function

Estimate the mass concentration using the inverse first order calibration equation (4) as follows:

$$\rho_i = \frac{Y_i - a_{o,i}}{b_i} \quad (4)$$

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

Take into account all of the dilution steps.

11.3 Calculation using the second order calibration function

Estimate the mass concentration using the inverse second order calibration equation (5) as follows:

$$\rho_i = -\frac{b_i}{2c_i} - \sqrt{\left(\frac{b_i}{2c_i}\right)^2 - \frac{a_{o,i} - Y_i}{c_i}} \quad (5)$$

For an explanation of the variables, see equations (2) and (3).

Take into account all of the dilution steps.

12 Expression of results

Report the results to a maximum of two significant figures.

EXAMPLE:

Sodium	(Na)	120	mg/l
Calcium	(Ca)	35	mg/l
Magnesium	(Mg)	1,5	mg/l

13 Test report

The test report shall contain the following information:

a) a reference to this International Standard;

b) identity of the water sample;

c) expression of the results according to clause 12;

d) description of sample pretreatment, if relevant;

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

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

g) calculation of the results (linear calibration function, method of standard addition);

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

Annex A
(informative)

Interlaboratory trial

An interlaboratory trial was organized in Germany in 1997 with laboratories from Switzerland and Germany participating. A variety of instruments and other analytical conditions were used conforming with the quality parameters specified in the method.

For the description of sample matrix see table A.1.

The statistical data for the results are presented in tables A.2 to A.10.

The coefficients of variation of the procedure V_{xo} (obtained from determined calibration functions analogous to those described in 10.2) are listed in table A.11. The data is from laboratories participating in the interlaboratory trial in Germany in 1997.

Table A.1 — Description of sample matrix

Matrix	Sample number						
	1	2	3	4	5	6	7
	Synthetic	Drinking water		River water		Sewage, domestic	
	Parameter (mg/l)						
TOC	< 1	< 1	< 1	2,7	2,3	9,4	9,7
SO_4	< 0,1	1,5	1,3	1,7	1,4	2,6	1,1
Cl	< 0,1	97	113	190	230	405	280
Pb	< 0,1	< 0,1	0,02	0,02	0,03	0,01	0,12
Ni	< 0,03	< 0,03	< 0,03	< 0,03	< 0,03	< 0,03	< 0,03
Cu	< 0,03	< 0,03	< 0,03	< 0,03	< 0,03	< 0,03	< 0,03
Cr	< 0,03	< 0,03	0,03	< 0,03	0,04	< 0,03	< 0,03
Cd	< 0,02	< 0,02	< 0,02	< 0,02	< 0,02	< 0,02	< 0,02
Zn	< 0,02	0,02	< 0,02	< 0,02	< 0,02	< 0,02	< 0,02
Fe	< 0,02	0,02	< 0,02	< 0,02	< 0,02	0,05	< 0,02
Si	< 0,1	5,8	1,5	3,3	0,9	6,9	1,7
Al	< 0,1	< 0,1	< 0,1	< 0,1	< 0,1	< 0,1	< 0,1
NH_4	0,25	0,55	1,1	0,5	1,1	1,7	10
Ba	2,1	2,5	3,4	3,3	5,5	2,9	7
Ca	1	91	114	101	122	67	86
K	0,2	2,4	8	7	25	27	37
Mg	1,2	16	27	15	20	16	38
Mn	1,1	1,1	19	2,5	29	4,8	37
Na	0,2	10	21	82	135	180	225
Sr	1,2	0,6	8,3	1,8	10	2,4	21

Table A.2 — Statistical data for ammonium

Sample No.	L	n	NA	KA_1 %	$\bar{x}$ mg/l	s_R mg/l	CV_R %	s_r mg/l	CV_r %
1	18	71	1	1,4	0,24	0,062	26,3	0,010	4,3
2	16	63	5	7,4	0,52	0,079	15,2	0,027	5,2
3	16	64	4	5,9	1,03	0,176	17,1	0,036	3,5
4	16	64	4	5,9	1,02	0,462	45,5	0,047	4,6
5	16	64	0	0	1,70	0,874	51,4	0,198	11,6
6	15	60	0	0	3,18	0,909	28,6	0,176	5,5
7	18	71	1	1,4	11,38	2,652	23,3	0,298	2,6

L is the number of participating laboratories;
n is the number of analytical values per level;
NA is the number of outlying 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.

Table A.3 — Statistical data for barium

Sample No.	L	n	NA	KA_1 %	$\bar{x}$ mg/l	s_R mg/l	CV_R %	s_r mg/l	CV_r %
1	14	56	0	0	1,93	0,208	10,8	0,103	5,3
2	14	56	0	0	2,17	0,241	11,1	0,136	6,2
3	12	47	4	7,8	3,04	0,210	6,9	0,119	3,9
4	14	56	0	0	3,24	0,253	7,8	0,103	3,2
5	14	56	0	0	5,00	0,605	12,1	0,381	7,6
6	14	55	0	0	2,87	0,270	9,4	0,115	4,0
7	14	55	1	1,8	6,51	0,642	9,9	0,207	3,2

NOTE For definition of symbols see table A.2.

Table A.4 — Statistical data for potassium

Sample No.	L	n	NA	KA_1 %	$\bar{x}$ mg/l	s_R mg/l	CV_R %	s_r mg/l	CV_r %
1	14	55	17	23,6	0,25	0,043	17,0	0,023	9,0
2	18	71	1	1,4	2,36	0,326	13,8	0,147	6,3
3	18	72	0	0	7,62	0,478	6,3	0,228	3,0
4	17	67	5	6,9	6,48	0,347	5,4	0,153	2,4
5	18	71	1	1,4	22,50	2,272	10,1	1,042	4,6
6	17	68	4	5,6	24,10	1,032	4,3	0,618	2,6
7	18	72	0	0	33,06	2,291	6,9	1,033	3,1

NOTE For definition of symbols see table A.2.

Table A.5 — Statistical data for calcium

Sample No.	L	n	NA	KA_1 %	$\bar{x}$ mg/l	s_R mg/l	CV_R %	s_r mg/l	CV_r %
1	16	63	9	12,5	0,91	0,077	8,5	0,033	3,6
2	19	75	1	1,3	82,73	5,484	6,6	2,683	3,2
3	19	76	0	0	105,10	6,042	5,8	1,580	1,5
4	18	72	4	5,3	93,85	5,526	5,9	1,075	1,2
5	18	72	4	5,3	111,20	5,398	4,9	1,358	1,2
6	17	68	8	10,5	62,80	3,122	5,0	0,853	1,4
7	18	72	4	5,3	79,30	3,000	3,8	1,412	1,8

NOTE For definition of symbols see table A.2.

Table A.6 — Statistical data for lithium

Sample No.	L	n	NA	KA_1 %	$\bar{x}$ mg/l	s_R mg/l	CV_R %	s_r mg/l	CV_r %
1	17	68	0	0	0,025	0,004	17,9	0,002	8,6
2	16	63	5	7,4	0,56	0,018	3,1	0,008	1,4
3	16	64	4	5,9	1,09	0,049	4,5	0,024	2,2
4	15	60	8	11,8	1,26	0,047	3,7	0,029	2,3
5	16	64	4	5,9	2,11	0,152	7,2	0,051	2,4
6	16	64	4	5,9	0,86	0,039	4,5	0,020	2,4
7	15	60	8	11,8	1,88	0,089	4,7	0,058	3,1

NOTE For definition of symbols see table A.2.

Table A.7 — Statistical data for magnesium

Sample No.	L	n	NA	KA_1 %	$\bar{x}$ mg/l	s_R mg/l	CV_R %	s_r mg/l	CV_r %
1	16	64	8	11,1	1,09	0,059	5,4	0,028	2,5
2	18	71	5	6,6	15,56	0,905	5,8	0,365	2,4
3	17	68	4	5,6	25,81	1,635	6,3	0,923	3,6
4	18	72	4	5,3	13,86	0,974	7,0	0,444	3,2
5	17	68	4	5,6	18,77	1,493	8,0	0,718	3,8
6	19	76	0	0	15,57	1,246	8,0	0,627	4,0
7	18	72	0	0	36,27	2,135	5,9	0,602	1,7

NOTE For definition of symbols see table A.2.