
**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 résiduelles*

(standards.iteh.ai)

ISO 14911:1998

<https://standards.iteh.ai/catalog/standards/sist/8ae1ab17-bf0b-4937-8b75-70f7f3788c07/iso-14911-1998>



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*.

ISO 14911:1998

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

<https://standards.iteh.ai/catalog/standards/sist/8ae1ab17-bf0b-4937-8b75-7017b788c07/iso-14911-1998>

© ISO 1998

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

International Organization for Standardization
Case postale 56 • CH-1211 Genève 20 • Switzerland
Internet iso@iso.ch

Printed in Switzerland

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.

iTeh STANDARD PREVIEW
(standards.iteh.ai)

ISO 14911:1998

<https://standards.iteh.ai/catalog/standards/sist/8ae1ab17-bf0b-4937-8b75-70f7f3788c07/iso-14911-1998>

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

ISO 14911:1998

<https://standards.iteh.ai/catalog/standards/sist/8ae1ab17-bf0b-4937-8b75-70f7f3788c07/iso-14911-1998>

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 Zn²⁺, Ni²⁺, Cd²⁺ 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 NH₄⁺ 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⁺, NH₄⁺, K⁺, Mn²⁺, Ca²⁺, Mg²⁺, Sr²⁺ and Ba²⁺ 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 ± 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 $\pm 1\%$ 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), $\text{C}_3\text{H}_8\text{N}_2\text{O}_2 \cdot \text{HCl}$.

6.2 Hydrochloric acid solution, $c(\text{HCl}) = 7,7$ mol/l.

6.3 Methanesulfonic acid, $\text{CH}_3\text{SO}_3\text{H}$ ($\geq 99\%$).

6.4 Pyridine 2,6-dicarboxylic acid (PDA), $\text{C}_7\text{H}_5\text{NO}_4$.

6.5 Tartaric acid, $\text{C}_4\text{H}_6\text{O}_6$.

6.6 Nitric acid solution, $c(\text{HNO}_3) = 1$ 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, $\text{Mn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$.

6.12 Calcium nitrate tetrahydrate, $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$.

6.13 Magnesium nitrate hexahydrate, $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$.

6.14 Strontium nitrate, $\text{Sr}(\text{NO}_3)_2$.

6.15 Barium nitrate, $\text{Ba}(\text{NO}_3)_2$.

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 $\pm$ 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 $\pm$ 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 $\pm$ 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 $\rho = 1000 \text{ mg/l}$ 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	$9,933\ 7 \pm 0,099$	Dry at $105^\circ\text{C} \pm 5^\circ\text{C}$, 2 h	in 0,001 mol/l HNO_3 ²⁾
Sodium	NaNO_3	$3,697\ 9 \pm 0,037$	Dry at $105^\circ\text{C} \pm 5^\circ\text{C}$	in water
Ammonium	NH_4Cl	$2,965\ 5 \pm 0,030$	Dry at $105^\circ\text{C} \pm 5^\circ\text{C}$	in water
Potassium	KNO_3	$2,586\ 0 \pm 0,026$	Dry at $105^\circ\text{C} \pm 5^\circ\text{C}$	in water
Manganese	$\text{Mn}(\text{NO}_3)_2 \cdot 4 \text{H}_2\text{O}$	$4,569\ 0 \pm 0,046$ ³⁾	Dry in a desiccator	in 0,001 mol/l HNO_3 ²⁾
Calcium	$\text{Ca}(\text{NO}_3)_2 \cdot 4 \text{H}_2\text{O}$	$5,892\ 0 \pm 0,059$ ³⁾	Dry in a desiccator	in 0,001 mol/l HNO_3 ²⁾
Magnesium	$\text{Mg}(\text{NO}_3)_2 \cdot 6 \text{H}_2\text{O}$	$10,549\ 7 \pm 0,105$ ³⁾	Dry in a desiccator	in 0,001 mol/l HNO_3 ²⁾
Strontium	$\text{Sr}(\text{NO}_3)_2$	$2,415\ 3 \pm 0,024$	Dry at $105^\circ\text{C} \pm 5^\circ\text{C}$	in 0,001 mol/l HNO_3 ²⁾
Barium	$\text{Ba}(\text{NO}_3)_2$	$1,903\ 1 \pm 0,019$	Dry at $105^\circ\text{C} \pm 5^\circ\text{C}$	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 necessary 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):

- eluent reservoir;
- pump, suitable for HPLC;
- sample injection system incorporating a sample loop (e.g. sample loop of volume 10 µl);
- precolumn (see 10.3.1) e.g. containing the same resin material as the analytical separator column or packed with a macroporous polymer;
- separator column with the specified separating performance (see clause 8);
- conductivity detector (with or without a suppressor device assembly);
- recording device;
- 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 NH₄⁺, 2 mg/l K⁺, Mn²⁺, Ca²⁺ or Mg²⁺, 5 mg/l Sr²⁺ and 10 mg/l Ba²⁺ (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.