
**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*



Foreword

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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.

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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 $\pm 1\%$ 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, $\text{CH}_4\text{O}_3\text{S}$ ($\geq 99\%$).

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).