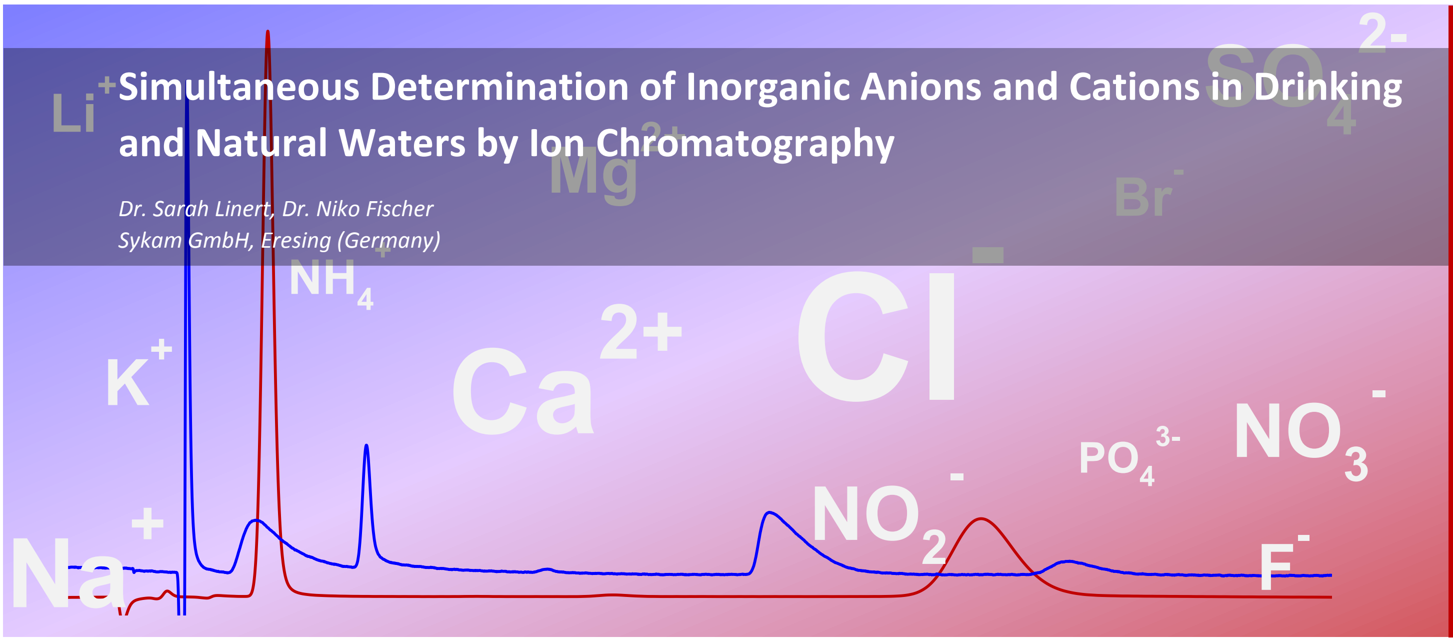

Simultaneous Determination of Inorganic Anions and Cations in Drinking and Natural Waters by Ion Chromatography

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Sykam Application Note 03

Introduction

Clean drinking water is one of the most important resources on the planet. Therefore, it is of utmost importance to ensure the quality of drinking water and to protect natural waters from pollution by industrial and other human sources. During the last decades this topic has attracted a great deal of attention all over the world and many governments have established regulations regarding the quality of drinking water. For instance, in the European Union, the Drinking Water Directive (DWD) 98/83/EC[1] from 1998 with its latest version 2020/2184[2] published in December 2020 is the respective guideline. The objectives of this directive are to protect human health from adverse effects of any contamination of water intended for human consumption. In the United States, water quality is legislated by the Safe Drinking Water Act (SDWA),[3] which ensures the integrity and safety of drinking waters. To protect natural water resources, the European Union established the Water Framework Directive 2000/60/EC[4] in October 2000, which forms the framework for the protection of inland surface waters, transitional waters, coastal waters and groundwater to prevent further deterioration and protect and enhance the status of aquatic ecosystems. The respective primary federal law in the United States is the Clean Water Act (CWA),[5] which is aimed to reduce discharge of pollutants into natural waters. The content of specific chemicals is regulated by Maximum Contaminant Levels (MCL) e.g. under the EU Drinking Water Directive (DWD)[2] or the U.S. National Primary and Secondary Drinking Water Standards (NPDWS/NSDWS).[6] In most parts of the world similar health and environmental standards have been established, often by adopting the aforementioned regulations.

Fluoride, nitrite and nitrate are considered primary contaminants in the U.S., while chloride and sulfate are secondary contaminants.[6] These anions are also listed in the EU Drinking Water Directive.[2] The common cations present in drinking and natural waters are not considered primary contaminants in the U.S., but they are monitored and reported by most suppliers and regulated in the EU. Calcium and magnesium are measured to determine the hardness of water. Ammonium is of special interest since it can dissociate to ammonia in water depending on temperature and pH. The degree of dissociation determines its toxicity to aquatic life.[7]

Ion chromatography (IC) is one of the most commonly used analytical techniques for the quantification of ionic species in drinking and natural waters. It has been validated and published as the standard method for the determination of anions by many national and international standard organizations like the ISO (International Organization for Standardization), the ASTM (American Society for Testing and Materials) or the AWWA (American Water Works Association) and also the U.S. EPA (Environmental Protection Agency of the U.S.). For the analysis of anions in drinking and natural waters, a considerable number of regulatory IC methods have been published worldwide, including the EN ISO 10304-1[8] (Technical Committee ISO/TC 147 “Water quality”), the EPA 300.1[9] or the ASTM D4327.[10] If used for cation analysis, IC allows the determination of alkaline and alkaline earth metals in a single run with ammonium. The methods for analysis of cations using IC are described in ASTM D6919[11] and EN ISO 14911.[12]

This application note “Sykam AN03” describes the simultaneous determination of inorganic anions and cations in drinking and natural waters by IC using suppressed conductivity measurement for anion detection. The method was validated under consideration of the requirements described in the abovementioned methods for anion and cation analysis and therefore provides an economical way to meet the testing requirements of EPA 300.1, Revision 1.0[9], EN ISO 10304-1:2009-07[8] and ASTM D4327-17[10] as well as ASTM D6919[11] and EN ISO 14911[12] using a Sykam S153 Dual IC module. The columns Sykam A07 (150 x 2.6 mm) and Sykam C07 (200 x 4.0 mm) were used for the method validation and the validation results are discussed within this application note.

SYKAM CHROMATOGRAPHY

Equipment

Application note Sykam AN03 is designed for use of a Sykam S153-AG Dual IC system with dual-channel anion and cation detection consisting of the following components:

- S150 Ion Chromatography Module including column oven, two-channel conductivity detectors and chemical anion suppressor module
- S1130 Quaternary Gradient Pump (PEEK) including 4-channel degasser
- S1130 Isocratic Pump (PEEK) including 1-channel degasser
- S5300 Automatic Sample Injector with S6165 injection valve (PEEK)
- S7150 Reagent Organizer with four eluent bottles (2 x 2000 mL, 2 x 1000 mL)
- Clarity advanced chromatography software for Windows (DataApex) or alternative data processing software.

The use of a second S1130 isocratic pump instead of an S1130 gradient pump is also possible.

Reagents and Standards

All reagents for eluent preparation and standards should be of analytical grade (ACS, p.a.) or better. We recommend the use of the following commercially available reagents. Alternatively, other reagents and standards can be used, if they are of comparable or better purity.

- Deionized water, Type I reagent grade, 0.1 µS/cm conductivity (10 kΩ/cm resistivity) or better
- Sodium carbonate (Na_2CO_3, anhydrous, for analysis, ACS, ISO, Reag. Ph Eur), Merck (1.06393)
- Sodium thiocyanate (NaSCN, ACS reagent, ≥98.0%), Sigma-Aldrich (251410)
- Oxalic acid dihydrate ($C_2H_2O_4 \cdot 2\,H_2O$, ReagentPlus®, ≥99.0%), Sigma-Aldrich (O0376)
- 2,6-Pyridinedicarboxylic acid ($C_7H_5NO_4$, 99%), Sigma-Aldrich (P63808)
- Fluoride standard solution (traceable to SRM from NIST, NaF in H_2O, 1000 mg/L F, Certipur®), Merck (1.19814)
- Chloride standard solution (traceable to SRM from NIST, NaCl in H_2O, 1000 mg/L Cl, Certipur®), Merck (1.19897)
- Nitrite standard solution (traceable to SRM from NIST, $NaNO_2$ in H_2O, 1000 mg/L NO_2, Certipur®), Merck (1.19899)
- Bromide standard solution (traceable to SRM from NIST, NaBr in H_2O, 1000 mg/L Br, Certipur®), Merck (1.19896)
- Nitrate standard solution (traceable to SRM from NIST, $NaNO_3$ in H_2O, 1000 mg/L NO_3, Certipur®), Merck (1.19811)
- Phosphate standard solution (traceable to SRM from NIST, KH_2PO_4 in H_2O, 1000 mg/L PO_4, Certipur®), Merck (1.19898)
- Sulfate standard solution (traceable to SRM from NIST, Na_2SO_4 in H_2O, 1000 mg/L SO_4, Certipur®), Merck (1.19813)
- Lithium standard solution (traceable to SRM from NIST, $LiNO_3$ in 0.5 mol/L HNO_3, 1000 mg/L Li, Certipur®), Merck (1.70223)
- Sodium standard solution (traceable to SRM from NIST, $NaNO_3$ in H_2O, 1000 mg/L Na, Certipur®), Merck (1.19507)
- Ammonium standard solution (traceable to SRM from NIST, NH_4Cl in H_2O, 1000 mg/L NH_4, Certipur®), Merck (1.19812)
- Potassium standard solution (traceable to SRM from NIST, KNO_3 in 0.5 mol/L HNO_3, 1000 mg/L K, Certipur®), Merck (1.70230)
- Calcium standard solution (traceable to SRM from NIST, $Ca(NO_3)_2$ in 0.5 mol/L HNO_3, 1000 mg/L Ca, Certipur®), Merck (1.19778)
- Magnesium standard solution (traceable to SRM from NIST, $Mg(NO_3)_2$ in 0.5 mol/L HNO_3, 1000 mg/L Mg, Certipur®), Merck (1.19788)

If the 1000 mg/L standard solutions are freshly prepared, we recommend the use of the following analytical or ACS reagent grade chemicals. Alternatively, other chemicals of comparable or better purity can be used. Anhydrous salts should be used for the preparation of standard solutions, if possible, since they can be dried in a vacuum oven if necessary. We recommend the use of sodium or potassium salts for the preparation of anion standard solutions, while chlorides or nitrates are the preferred salts for preparation of cation standard solutions.

- Sodium fluoride (NaF, for analysis EMSURE, Reag. Ph Eur), Merck (1.06449)
- Sodium chloride (NaCl, for analysis EMSURE, ACS, ISO, Reag. Ph Eur), Merck (1.06404)
- Sodium nitrite ($NaNO_2$, for analysis EMSURE, ACS, Reag. Ph Eur), Merck (1.06549)
- Sodium bromide (NaBr, ACS reagent, ≥99.0%), Sigma-Aldrich (310506)
- Sodium nitrate ($NaNO_3$, for analysis EMSURE, ACS, ISO, Reag. Ph Eur), Merck (1.06537)
- Potassium dihydrogen phosphate (KH_2PO_4, for analysis EMSURE, ISO), Merck (1.04873)
- Sodium sulfate (Na_2SO_4, anhydrous, for analysis EMSURE, ACS, ISO, Reag. Ph Eur), Merck (1.06649)
- Lithium nitrate ($LiNO_3$, anhydrous, extra pure, SLR), Fisher Chemical (10568620)
- Ammonium chloride (NH_4Cl, Suprapur®), Merck (1.01143)
- Potassium nitrate (KNO_3, ACS reagent, ≥99.0%), Sigma-Aldrich (221295)
- Calcium nitrate tetrahydrate ($Ca(NO_3)_2 \cdot 4\,H_2O$, for analysis EMSURE, ACS, ISO, Reag. Ph Eur), Merck (1.02121)
- Magnesium nitrate hexahydrate ($Mg(NO_3)_2 \cdot 6\,H_2O$, ACS reagent, 99%), Sigma-Aldrich (237175)

Samples

For the method validation, seven water samples were analyzed (Table 1).

Table 1. List of analyzed samples.

No.	Name
1	Drinking Water (Straubing)
2	Drinking Water (Hamlar)
3	Mineral Water 1
4	Mineral Water 2
5	Melted Snow
6	Stream Water (Staltannen)
7	Lake Water (Hamlar)

All seven water samples were collected in southern Germany in the northern foothills of the Alps, where lime containing soil is the prevailing geological formation. The two drinking water samples were collected as tap water from two different municipal water suppliers in Straubing and Hamlar. The two mineral water samples were commercially available mineral waters from companies, that obtain their water from natural ground water sources. For the melted snow sample, freshly fallen snow was collected in a beaker and allowed to warm up to ambient temperature. The stream water was collected from a stream near Staltannen and the lake water was collected from a ground water fed pond near Hamlar. All samples were collected in 1000 mL glass or PE-bottles with a screw cap and stored at 4 °C immediately after collection.

Chromatographic Conditions

Method Validation Anions

Columns:	Sykam A07 (150 x 2.6 mm), Analytical column Sykam AGC-04 (20 x 2.6 mm), Guard column
Eluent:	4.0 mM Na_2CO_3, 25 µM NaSCN
Flow Rate:	1.0 mL/min
Run Time:	17 min
Temperature:	40 °C
Injection Volume:	50 µL (full loop)
Detection:	Suppressed Conductivity, Sykam Chemical Anion Suppressor
Suppressor Speed:	80 rpm
Backpressure:	57 bar (830 psi)
Base Conductivity:	21 µS/cm
Noise:	<5 nS/cm

Method Validation Cations

Columns:	Sykam C07 (200 x 4.0 mm), Analytical column Sykam CGC-03 (50 x 4.6 mm), Guard column*
Eluent:	2.0 mM Oxalic acid, 3.5 µM 2,6-Pyridine-dicarboxylic acid
Flow Rate:	1.0 mL/min
Run Time:	17 min
Temperature:	40 °C
Injection Volume:	10 µL (full loop)
Detection:	Non-suppressed Conductivity (Inverted Signal)
Backpressure:	56 bar (810 psi)
Base Conductivity:	1140 µS/cm
Noise:	<50 nS/cm

* We recommend the use of the new CGC-07 guard column

All settings listed here are part of the chromatographic method and can be saved in the “Method Setup” window of the Clarity software. Since cation detection is non-suppressed, the cation signal needs to be inverted by clicking the box “Reverse Signal” in the “Acquisition” Tab of the “Method Setup” window to obtain positive peaks for integration.

To achieve reproducible results, only full loop injections were performed. In case of the dual analysis, both injection loops are connected in series, indicating, that an injection volume of at least 100 µL needs to be programmed in the sequence to fill both loops with 50% excess.

For cation analysis it is also possible to use the CGC-07 guard column (50 x 4.0 mm) instead of the CGC-03. For this method validation the CGC-03 was used, since the CGC-07 was not established at the time the experiments for this method validation were performed. The method for cation analysis using the C07 column with a CGC-07 guard column is described in application note AN05. We recommend the use of the CGC-07 as this guard column increases the resolution, but the method using the CGC-07 also has longer retention times and therefore a longer run time of 22 min is required.

Preparation of Solutions and Reagents

Standard Stock Solutions (1000 mg/L)

The standard stock solutions of the seven standard anions fluoride, chloride, nitrite, bromide, nitrate, phosphate and sulfate, and the six standard cations lithium, sodium, ammonium, potassium, calcium and magnesium can either be purchased from commercial sources as indicated in section “Reagents and Standards” or prepared from the respective salts, if commercial standard stock solutions are not available. The amounts needed for the preparation of 1000 mL of each standard stock solution are given in Table 2. Should only a few, and not all, of the standard ions need to be analyzed, the respective standard solutions can be omitted. The 1000 mg/L standard stock solutions are stable for at least one month when stored at 4 °C.

Table 2. Amounts of salts needed for preparation of 1000 mL of standard stock solutions (1000 mg/L).

Analyte	Compound	Amount (g)
Fluoride	Sodium fluoride (NaF)	2.210
Chloride	Sodium chloride (NaCl)	1.648
Nitrite	Sodium nitrite ($NaNO_2$)	1.500
Bromide	Sodium bromide (NaBr)	1.288
Nitrate	Sodium nitrate ($NaNO_3$)	1.371
Phosphate	Potassium dihydrogen phosphate (KH_2PO_4)	1.433
Sulfate	Sodium sulfate (Na_2SO_4)	1.479
Lithium	Lithium nitrate ($LiNO_3$)	9.933
Sodium	Sodium nitrate ($NaNO_3$)	3.697
Ammonium	Ammonium chloride (NH_4Cl)	2.965
Potassium	Potassium nitrate (KNO_3)	2.586
Calcium	Calcium nitrate tetrahydrate ($(Ca(NO_3)_2 \cdot 4\ H_2O)$)	5.892
Magnesium	Magnesium nitrate hexahydrate ($(Mg(NO_3)_2 \cdot 6\ H_2O)$)	10.547

Working Standard Solutions

All single and mixed working standard solutions at concentrations lower than 1000 mg/L are prepared from the standard stock solutions and should be prepared fresh daily. A series of mixed standards at concentrations of 200, 100, 50, 20, 10 and 5 µg/L of each anion is prepared from 10 mg/L single standard solutions for the preliminary estimation of the method detection limit. For the estimation of the method detection limits of the cations a series of mixed standards at concentrations of 500, 400, 300, 200, 100, 50 and 20 µg/L of each cation is prepared from 10 mg/L single standard solutions.

Table 3 gives the concentrations of the standards prepared to calculate the method detection limits (MDL_S) as well as the concentrations of the Quality Control Samples (QCS), which are analyzed to determine retention time stability and peak area precision of the instrument.

The determination of the linear calibration range of the seven standard anions covering the expected concentrations of the drinking and natural water samples is achieved by injecting ten levels of calibration of a mixed anion standard at the following concentrations: 0.1, 0.2, 0.5, 1.0, 2.0, 5.0, 10, 20, 50 and 100 mg/L (0.02 – 20 mg/L for fluoride). All concentration levels are prepared from the 1000 mg/L standard stock solutions. For the determination of the linear calibration range of the six standard cations covering the expected concentrations of the drinking and natural water samples seven levels of calibration of a mixed cation standard were injected. The concentration levels were 2, 4, 10, 20, 40, 60 and 100% of the maximum cation standard concentration as listed in Table 3. All concentration levels are prepared from the 1000 mg/L standard stock solutions.

Table 3. Concentrations of $\mathrm{MDL_S}$, QCS and 100% linearity standard.

Analyte	$\mathrm{MDL_S}$ Calculation Standard Anions (µg/L)	QCS for Precision Anions (mg/L)	Maximum Standard Concentration Anions (mg/L)
Fluoride	10	2	20
Chloride	10	10	100
Nitrite	50	2	100
Bromide	80	2	100
Nitrate	100	20	100
Phosphate	500	2	100
Sulfate	250	30	100
Analyte	**$\mathrm{MDL_S}$ Calculation Standard Cations (µg/L)**	**QCS for Precision Cations (mg/L)**	**Maximum Standard Concentration Cations (mg/L)**
Lithium	500	2	2
Sodium	100	15	50
Ammonium	1000	5	10
Potassium	2000	10	20
Calcium	2000	40	50
Magnesium	2000	20	30

To assess the performance of the chromatographic system, External Control Samples (ECS) are prepared at the same concentration as the QCS. To prepare the ECS, 1000 mg/L stock solutions are prepared from chemicals other than the standard stock solutions used for the determination of the linear calibration range. The amounts to be used are given in Table 2.

Eluent solutions

The eluents are prepared from eluent stock solutions with concentrations of 1.00 mol/L. For the sodium carbonate stock solution 53.00 g of Na_2CO_3 are dissolved in 400 mL of deionized water in a 500 mL volumetric flask. The solution is mixed thoroughly until completely clear and the flask is filled up to the mark once the solution has reached room temperature. For the sodium thiocyanate stock solution 4.054 g of NaSCN are dissolved in 40 mL of deionized water in a 50 mL volumetric flask in the same manner, and the flask is filled to the mark. For the oxalic acid stock solution 12.61 g of oxalic acid dihydrate are dissolved in 80 mL of deionized water in a 100 mL volumetric flask in the same manner, and the flask is filled to the mark.

For the chromatographic system discussed here, the following eluents are prepared:

Anions (Sykam A07): 4.0 mM Na_2CO_3, 25 µM NaSCN – 8.0 mL of the 1.0 mol/L Na_2CO_3 stock solution as well as 50 µL of the 1.0 mol/L NaSCN stock solution are added to 2000 mL of deionized water. The solution is mixed thoroughly and filtered over a 0.45 µm regenerated cellulose filter disc. The eluent is transferred to the S7150 Reagent Organizer and the container is pressurize with inert gas (optional).

Cations (Sykam C07): 2.0 mM oxalic acid, 3.5 mM 2,6-pyridinedicarboxylic acid – 4.0 mL of the 1.0 mol/L oxalic acid stock solution and 1169.8 mg of 2,6-pyridinedicarboxylic acid are added to 2000 mL of deionized water. The solution is mixed thoroughly until the solid is dissolved completely. Then it is filtered over a 0.45 µm regenerated cellulose filter disc. The eluent is transferred to the S7150 Reagent Organizer and the container is pressurize with inert gas (optional).

Preparation of the IC system

If using new columns, install the columns and condition them at a flow rate of 0.3 mL/min of the respective eluent before slowly increasing the flow rate to the desired value of 1.0 mL/min. To achieve reproducible results, the system and especially the chemical suppressor unit, have to warm up and be equilibrated. For equilibration, switch on the column oven and the suppressor at the respective conditions. Apply the desired flow rate until the baseline has stabilized. The baseline noise should be <5.0 nS/cm for the anion channel and <50 nS/cm for the cation channel. If the system is used on a daily basis, leave the column oven as well as the suppressor unit switched on overnight and apply a low flow rate (0.1 mL/min), so that the system can readily be used for the following analyses. The suppressor speed can be reduced to 20 rpm overnight. Make sure, that the deionized water for washing of the automatic sample injector is sufficiently filled and perform two washing steps each at the injection port as well as at the washing port prior to analysis. During analysis, one washing step each at both ports is recommended after each injection. For more detailed instructions, refer to the corresponding installation, maintenance and operating manuals.

Sample Preparation

All drinking and natural water samples were degassed under vacuum for approx. 10 minutes prior to analysis. In the laboratory the samples were divided into an initial sample and a laboratory duplicate. The duplicate sample was treated identical to the initial sample to control the precision of the laboratory procedures. Samples have to be filtered through an appropriate syringe filter (0.45 µm regenerated cellulose) discarding the first 1.0 mL of the filtrate. To prevent nitrification and denitrification in the samples by microbial activity, changing the analyzed content of nitrite and nitrate, the samples must be stored at 4 °C and analyzed within 24 hours after collection.

Results and Discussion

The method validation for the determination of inorganic anions in drinking and natural waters was performed according to EPA method 300.1 (Revision 01),[9] as well as ISO EN 10304-1:2009-07[8] and ASTM D4327-17[10] ensuring that all requirements of these methods regarding quality control parameters are met. As defined by the methods, optional columns and corresponding, different chromatographic conditions may be used to improve separation or lower the cost of measurement. Here, the Sykam A07 column together with the Sykam S153-AG Dual IC module under the chromatographic conditions listed above were used for the validation. All required quality control parameters were tested including the determination of method detection limits MDL_S and MDL_B,[13] Linearity (Linear Calibration Range, LCR),[14] Precision by repeated injection of a Quality Control Sample (QCS), verification of the calibration standards and instrument performance by injection of an External Control Sample (ECS), laboratory performance by injection of a laboratory reagent blank (LRB) and laboratory fortified blank (LFB), analysis of field duplicates, and assessing analyte recovery by injection of Laboratory Fortified Matrices (LFM) for each sample. Instrument performance was checked throughout the entire sequence by analysis of initial, continuing and end calibration check standards.

The Sykam A07 is a high-capacity anion exchange column based on trimethylammonium functionalized PS-DVB with a particle size of 10 µm. Figure 1 shows the separation of a low-mg/L inorganic anion standard using the Sykam A07.

Column: Sykam A07 (150 x 2.6 mm) and Sykam AGC-04 (20 x 2.6 mm)
Eluent: 4.0 mM Na_2CO_3, 25 µM NaSCN
Flow Rate: 1.0 mL/min
Inj. Vol.: 50 µL
Detection: Suppressed Conductivity, Sykam Chemical Anion Suppressor (80 rpm)
Peaks: 1. Fluoride 1.0 mg/L
2. Chloride 5.0
3. Nitrite 5.0
4. Bromide 5.0
5. Nitrate 5.0
6. Phosphate 5.0
7. Sulfate 5.0

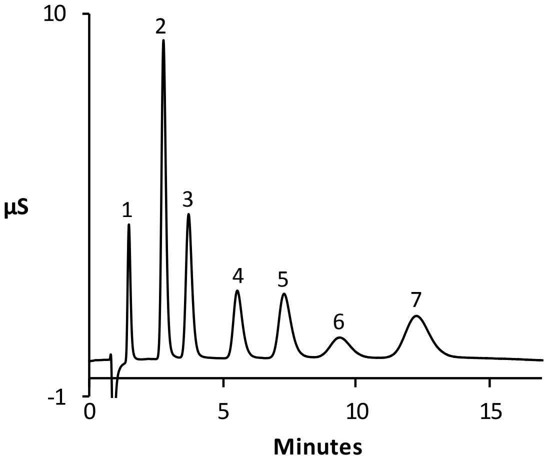

Figure 1. Separation of the 5% calibration standard for inorganic anions.

The peak resolution is R >1.3 for all standard anions (Table 4), as required in the method performance section of ISO EN 10304-1.[8] The column exhibits excellent peak symmetry, which allows exact integration of peak areas, as all peaks are baseline-separated.

Table 4. Column performance parameters of Sykam A07 (5% calibration standard) and Sykam C07 (10% calibration standard) at the chromatographic conditions listed above.

Analyte	Retention time (min)	Resolution R	Peak Symmetry
Fluoride	1.49	–	1.38
Chloride	2.79	5.01	1.25
Nitrite	3.73	2.57	1.28
Bromide	5.56	3.49	1.29
Nitrate	7.31	2.40	1.31
Phosphate	9.40	1.86	1.14
Sulfate	12.27	1.84	1.15
Lithium	3.18	–	1.36
Sodium	4.11	4.70	1.67
Ammonium	4.63	2.10	1.61
Potassium	6.49	5.74	1.20
Calcium	9.98	5.68	1.63
Magnesium	13.35	3.31	1.65

The method validation for the determination of cations in drinking and natural waters was performed according to the regulations listed in ASTM D6919[11] and EN ISO 14911.[12] The Sykam C07 is a weak cation exchange column based on a functionalized EVB-DVB resin with a particle size of 7 µm. Figure 2 shows the separation of an inorganic cation standard using the Sykam C07.

Column: Sykam C07 (200 x 4.0 mm) and Sykam CGC-03 (50 x 4.6 mm)
Eluent: 2.0 mM Oxalic acid, 3.5 mM 2,6-Pyridine-dicarboxylic acid
Flow Rate: 1.0 mL/min
Inj. Vol.: 10 µL
Detection: Non-suppressed Conductivity
Peaks: 1. Lithium 0.4 mg/L
2. Sodium 10.0
3. Ammonium 2.0
4. Potassium 4.0
5. Calcium 10.0
6. Magnesium 6.0

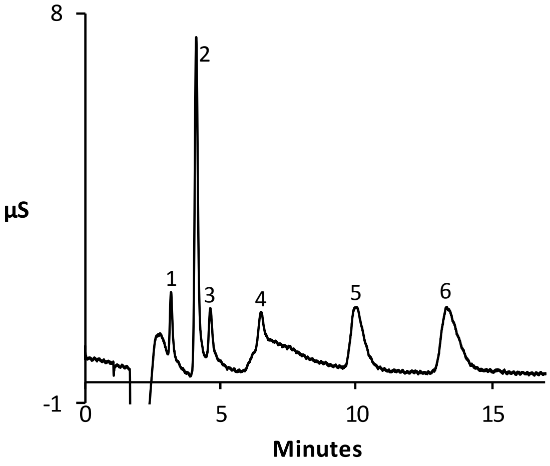

Figure 2. Separation of the 20% calibration standard for inorganic cations.

Method Detection Limits MDL_S and MDL_B

First the method detection limits based on sample injection (MDL_S) were estimated. Therefore, six mixed anion standards with the following concentrations were injected: 200, 100, 50, 20, 10 and 5 µg/L for each anion. The same procedure was used to determine the MDL_S of the cations, injecting seven mixed cation standards with concentrations of 500, 400, 300, 200, 100, 50 and 20 µg/L per cation. For each ion, the concentration, at which the signal-to-noise ratio is between 3 and 5 was determined or extrapolated. The estimated method detection limits were multiplied by a factor of 5 to obtain the final concentrations of the MDL$_S$-Calculation standards (Table 3). The MDL$_S$ for each ion was determined by performing seven replicate injections of the MDL$_S$-Calculation standards for anions and cations respectively. The MDL$_S$ was then calculated as $\mathrm{MDL}_S = t \times SD$, where t is the Student´s value for a 99% confidence level and a standard deviation estimate with n-1 degrees of freedom (t = 3.142613 for seven replicates) and SD is the standard deviation of the replicate analysis of the MDL$_S$-Calculation standard for each ion. The thus obtained method detection limits are listed in Tables 5 and 6 for the anions and cations respectively. In contrast to the MDL$_S$, the MDL$_B$ is based on the injection of blanks. It applies, if the injection of the Laboratory Reagent Blank (LRB) gives a numerical result for one of the investigated ions. In this case, seven replicates of the LRB were analyzed with the result that chloride was found at a mean level of 5.7 µg/L and sodium at a mean level of 0.40 mg/L. None of the other inorganic ions were found in any of the LRB injections. Therefore, for chloride and sodium, the method detection limit MDL$_S$ does not apply and the MDL$_B$ is calculated instead: $\mathrm{MDL}_B = X + t \times SD$, where X is the mean of the LRB results.[12] t is again 3.142613 for seven replicates and SD is the standard deviation of the replicate analysis of the LRB. The MDL$_B$ for chloride was calculated to 12.2 µg/L and the MDL$_B$ for sodium to 0.65 mg/L. The relatively high content of sodium in the LRB, and thus the high MDL$_B$, can be explained by a carryover of traces of the anion eluent to the cation system in the sample injection system. For the determination of low concentrations of sodium, we recommend the use of a S150+ IC module in single-channel cation detection mode with an electrochemical self-regenerating cation suppressor.

Linearity (LCR)

To assess the linear calibration range for each anion, mixed anion standards at ten calibration levels were injected: 0.1, 0.2, 0.5, 1.0, 2.0, 5.0, 10, 20, 50 and 100 mg/L. For the assessment of the linear calibration range of cations mixed cation standards at seven calibration levels were injected: 2, 4, 10, 20, 40, 60 and 100% of the maximum cation standard concentration. For quantification of the samples and the fortified samples, the calibration range was limited to its linear range individually for each ion. Therefore, only the calibration levels, that were found to be in a linear range, were used to assess the calibration curve individually for each ion. Figure 3 shows the linear calibration plots for all ions. Calibration points, that are outside the linear range, were omitted and are displayed in red. Chloride and nitrite exhibit a linear range of up to 100 mg/L, whereas bromide, nitrate, phosphate and sulfate were calibrated up to a maximum calibration level of 50 mg/L. For fluoride the calibration range was determined to 0.02–20 mg/L, which is sufficiently high, since fluoride in most drinking and natural water samples is contained in trace amounts <1.0 mg/L. Sodium and calcium exhibit a linear calibration range of 1.0–50 mg/L. Magnesium was calibrated in a concentration range of 0.6–30 mg/L. Concentrations of alkaline earth metals higher than those chosen for this calibration exceed the capacity of the Sykam C07 and impair the recovery of the alkaline metals, especially lithium. For the calibration of potassium, only six calibration levels were used, covering the range of 0.8–20 mg/L, because the concentration of 0.4 mg/L in the lowest concentrated calibration standard was below the MDL$_S$. The content of lithium and ammonium in drinking and natural water samples is expected to be in the low single digit mg/L or sub-mg/L range and therefore smaller concentration ranges of 0.04–2 mg/L and 0.2–6 mg/L respectively were used for the determination of these cations. In tables 5 and 6 the linear calibration ranges as well as the correlation factors r^2 of the linear fits for all ions are listed. All linear fits exhibit correlation factors of r^2 >0.999 and are considered very accurate.

Table 5. Linearity, MDL$_S$, retention time and peak area precision for the standard anions.

Analyte	Calibration range (mg/L)	Linearity (r^2)	Calculated MDL$_S$ (µg/L)	Retention Time Precision (RSD, %)	Peak Area Precision (RSD, %)
Fluoride	0.02 – 20	0.9998	2.4	0.40	0.24
Chloride	0.1 – 100	0.9997	4.2*	0.22	0.28
Nitrite	0.1 – 100	0.9997	6.8	0.16	0.54
Bromide	0.1 – 50	0.9998	20.4	0.14	0.44
Nitrate	0.1 – 50	0.9998	47.7	0.12	0.60
Phosphate	0.1 – 50	0.9998	50.3	0.24	0.93
Sulfate	0.1 – 50	0.9999	44.0	0.04	0.30

* Value not valid, MDL$_B$ is used instead

Table 6. Linearity, MDL$_S$, retention time and peak area precision for the standard cations.

Analyte	Calibration range (mg/L)	Linearity (r^2)	Calculated MDL$_S$ (µg/L)	Retention Time Precision (RSD, %)	Peak Area Precision (RSD, %)
Lithium	0.04 – 2	0.9994	29.0	0.16	0.65
Sodium	1 – 50	0.9996	47.2*	0.09	0.85
Ammonium	0.2 – 6	0.9998	61.3	0.13	0.97
Potassium	0.8 – 20	0.9999	536.9	0.16	0.82
Calcium	1 – 50	1.0000	655.0	0.12	0.90
Magnesium	0.6 – 30	0.9999	275.7	0.15	0.47

* Value not valid, MDL$_B$ is used instead

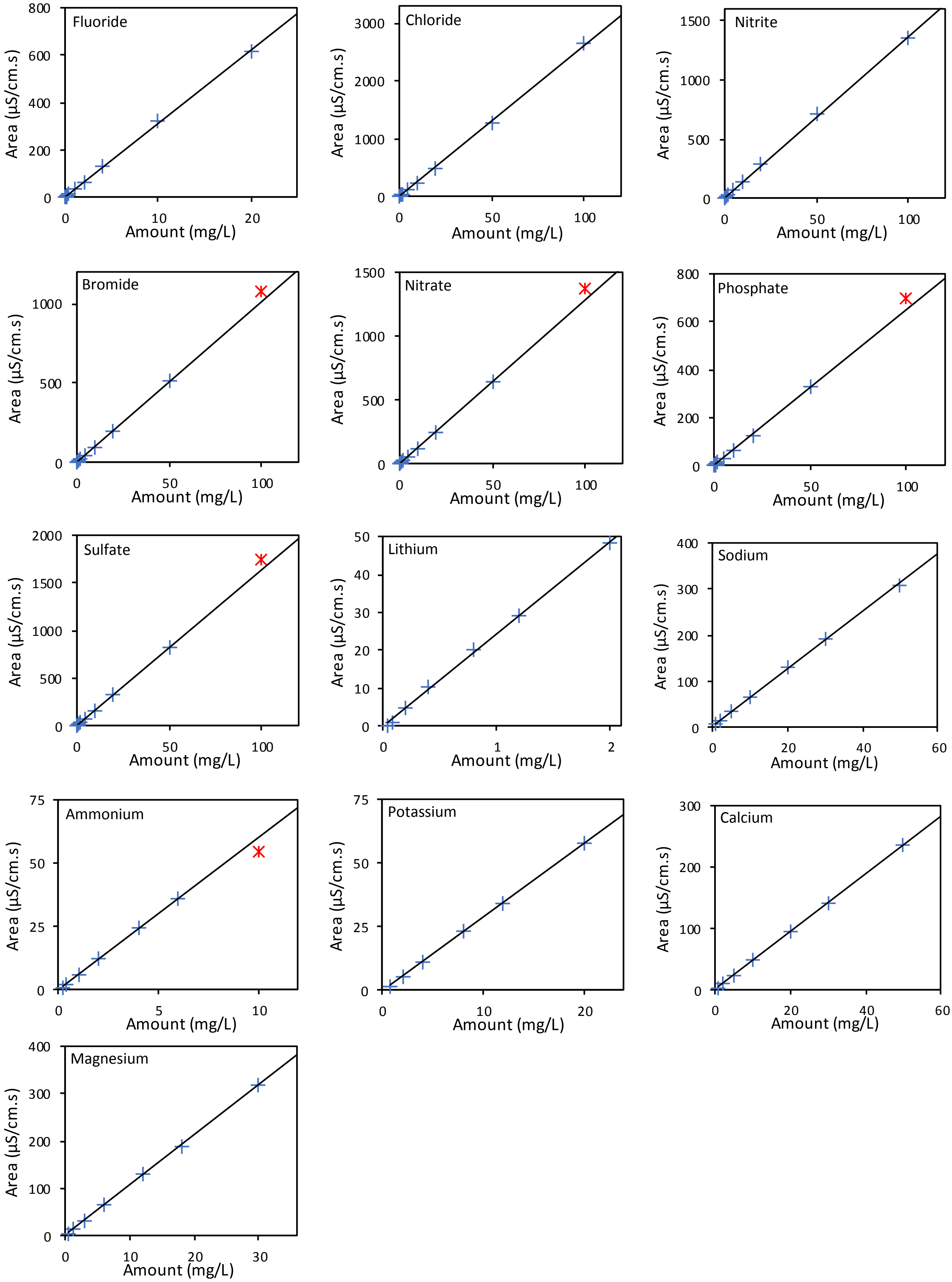

Figure 3. Calibration plots of the standard anions and cations indicating the LCR used for analysis of the samples.

Precision (QCS) and Instrument Performance (ECS)

Retention time and peak area precision were determined from seven replicate injections of a Quality Control Standard (QCS). Ideally, the concentrations of the single inorganic ions in the QCS are very similar to those found in the field samples. Their concentrations are listed in Table 3. Tables 5 and 6 show the results of the Relative Standard Deviation (RSD) of the retention time and peak area after seven replicate injections of the QCS. The RSD of the retention time is well below 1.0% and the RSD of the peak area was found to be considerably less than 2.0% for all investigated ions, illustrating the high precision reached with the Sykam S153-AG Dual IC system using the Sykam A07 and Sykam C07 columns. If no new calibration is performed prior to analysis, the calibration standards and acceptable instrument performance are verified by the preparation and analysis of a QCS. In this case, a new calibration was performed and the instrument performance was verified by the analysis of an External Calibration Standard (ECS). The ECS is prepared from 1000 mg/L single anion standard stock solutions, which are prepared from a different source than the standard stock solutions used for the calibration. The QCS, however is prepared from the same standard stock solutions that were used for the preparation of the calibration standards. If used for verification of instrument performance, the acceptance range for the Relative Percent Differences (RPD) between the ECS and the QCS is ±15%.[9] In table 7 the Relative Percent Difference (RPD) of the ECS prepared from the external source stock solutions and the QCS prepared from the stock solutions of the calibration are listed. The determined differences are well within the specified deviation range of ±15%.[9]

Table 7. Relative Percent Differences (RPD) of QCS and ECS.

Analyte	RPD (%)
Fluoride	0.0
Chloride	-1.6
Nitrite	-0.4
Bromide	-2.9
Nitrate	0.8
Phosphate	-0.6
Sulfate	-2.1
Lithium	-2.1
Sodium	1.7
Ammonium	2.8
Potassium	2.0
Calcium	2.1
Magnesium	-4.1

Sample Analysis

All seven samples (Table 1) were analyzed twice, undiluted after filtration, each as initial sample and laboratory duplicate. The anion contents of all samples were covered by the calibration ranges as defined above, but the calcium contents of the two drinking water samples, as well as the stream water and the lake water were higher than the highest calibration level. Therefore, these samples were diluted in a 1:1 ratio with deionized water and the analysis was repeated with the diluted samples to obtain valid results for cation analysis.

The melted snow sample (5) differs significantly from all other samples. As expected, only very low concentrations of any of the analytes could be detected. Only chloride, nitrate and ammonium could be quantified in small amounts <1.0 mg/L, while sulfate and sodium were detected at concentrations below the Minimum Reporting Level (MRL). The MRL is defined as the lowest concentration, at which an analyte can be quantified. The MRL is higher or equal to the lowest calibration concentration and higher than the MDL.[9] Table 8 gives an overview of the MRLs for each ion based on the applied linear calibration range and the calculated MDLs.

Table 8. Minimum Reporting Levels based on the LCR and MDL.

Analyte	MRL (mg/L)
Fluoride	0.02
Chloride	0.10
Nitrite	0.10
Bromide	0.10
Nitrate	0.10
Phosphate	0.10
Sulfate	0.10
Lithium	0.04
Sodium	1.0
Ammonium	0.20
Potassium	0.80
Calcium	1.0
Magnesium	0.60

Nitrite and phosphate were detected in none of the other six drinking and natural water samples (1–4, 6, 7), while bromide, if detected, was found only at very low concentrations below the MRL. Fluoride was found in low contents of 0.07–0.33 mg/L. Sulfate was found at a low concentration of 1.7 mg/L in the stream water sample (6), while in the other samples a significantly higher content was found ranging from 10.3 – 42.2 mg/L. The highest amounts of nitrate were found in the drinking water samples (23.6 mg/L and 9.9 mg/L). In the natural and mineral water samples the content of nitrate was <5 mg/L. The contents of chloride range from near the MRL up to more than 40 mg/L.

Lithium and ammonium were not detected in any of the drinking and natural water samples (1–4, 6, 7), while potassium was found only at very low concentrations <2.0 mg/L. The detected concentrations of magnesium cover the whole calibration range. The contents of sodium range from near the MRL up to more than 30 mg/L. Calcium was found at concentrations above 25 mg/L in all of these six samples.

Table 9 summarizes the found results for mineral water 1 and 2. The values are compared to the supplier's analysis results printed on the bottle label of each mineral water. For mineral water 1 the determined values correspond well with the analysis results given by the supplier as shown in table 9. The analysis results of mineral water 2 are also very similar to those found during this validation. The supplier's analysis report of mineral water 2 dates back to 2003 and therefore the concentrations of fluoride and chloride in this mineral water might differ slightly from the values found at that time.

Column: Sykam A07 (150 x 2.6 mm) and Sykam AGC-04 (20 x 2.6 mm)

Eluent: 4.0 mM Na_2CO_3, 25 µM NaSCN
Flow Rate: 1.0 mL/min
Inj. Vol.: 50 µL
Detection: Suppressed Conductivity, Sykam Chemical Anion Suppressor (80 rpm)
Peaks: 1. Fluoride 0.33 mg/L
2. Chloride 44.8
3. Bromide 0.07 (< MRL)
4. Nitrate 23.6
5. Sulfate 31.5

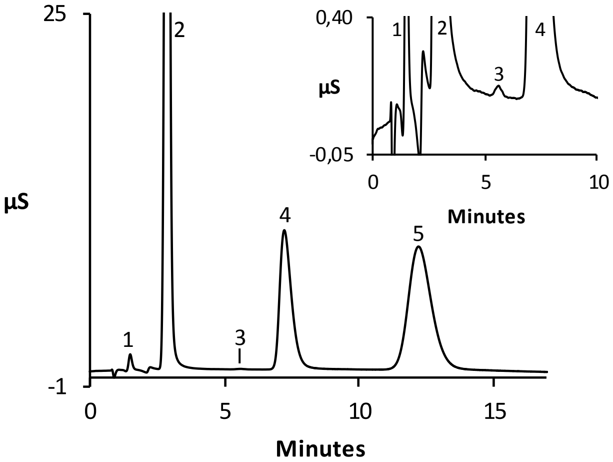

Figure 4. Determination of anions in drinking water (Straubing).

Column: Sykam A07 (150 x 2.6 mm) and Sykam AGC-04 (20 x 2.6 mm)
Eluent: 4.0 mM Na_2CO_3, 25 µM NaSCN
Flow Rate: 1.0 mL/min
Inj. Vol.: 50 µL
Detection: Suppressed Conductivity, Sykam Chemical Anion Suppressor (80 rpm)
Peaks: 1. Fluoride 0.12 mg/L
2. Chloride 0.43
3. Nitrate 0.02 (< MRL)
4. Sulfate 10.3

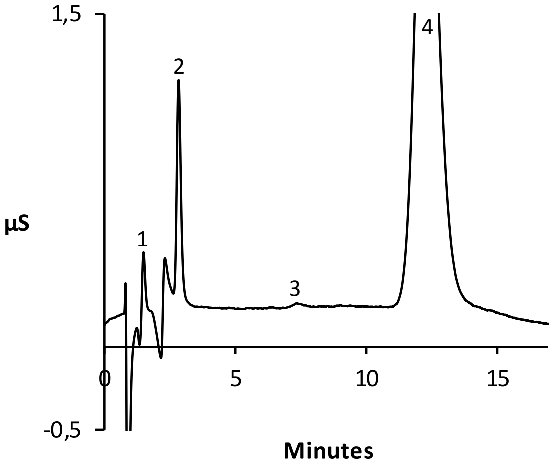

Figure 6. Determination of anions in mineral water 2.

Column: Sykam C07 (200 x 4.0 mm) and Sykam CGC-03 (50 x 4.6 mm)
Eluent: 2.0 mM Oxalic acid, 3.5 mM 2,6-Pyridine-dicarboxylic acid
Flow Rate: 1.0 mL/min
Inj. Vol.: 10 µL
Detection: Non-suppressed Conductivity
Peaks: 1. Sodium 35.3 mg/L
2. Potassium 1.9
3. Calcium 41.5
4. Magnesium 11.6

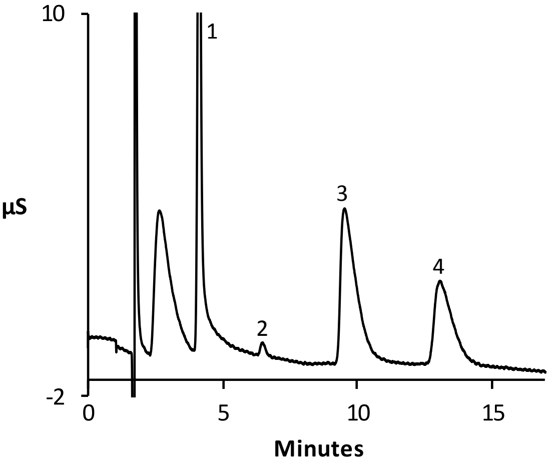

Figure 5. Determination of cations in drinking water (Straubing).

Column: Sykam C07 (200 x 4.0 mm) and Sykam CGC-03 (50 x 4.6 mm)
Eluent: 2.0 mM Oxalic acid, 3.5 mM 2,6-Pyridine-dicarboxylic acid
Flow Rate: 1.0 mL/min
Inj. Vol.: 10 µL
Detection: Non-suppressed Conductivity
Peaks: 1. Sodium 8.7 mg/L
2. Potassium 0.87
3. Calcium 43.0
4. Magnesium 21.6

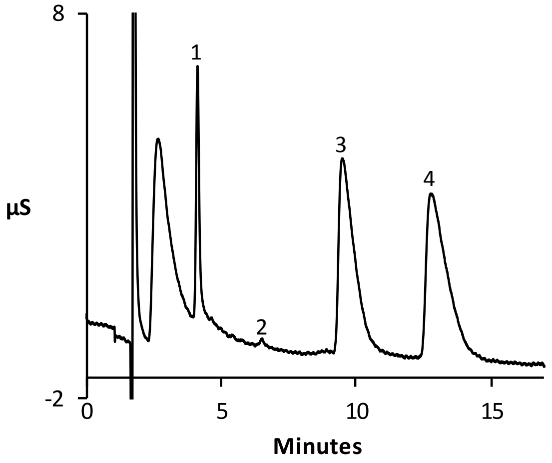

Figure 7. Determination of cations in mineral water 2.

Table 9. Analysis results during method validation (mg/L) and reported analysis results (mg/L) from suppliers of mineral waters.

Analyte	Mineral Water 1		Mineral Water 2	
	Method Validation	Supplier	Method Validation	Supplier
Fluoride	0.15		0.12	0.08
Chloride	18.4	20	0.43	1.6
Nitrate	0.29		< MRL	<0.5
Sulfate	22.2	19	10.3	11.7
Sodium	15.4	15	8.7	7.3
Potassium	1.6		0.87	0.9
Calcium	49.9	51	43.0	43.0
Magnesium	4.8	5.3 (-9.6)	21.6	21.0

The values found in the laboratory duplicates do not differ significantly from the respective initial samples, which indicates the robustness of the validated method. The required Relative Percent Difference (RPD) for duplicate analyses according to EPA 300.1 is ±20% for concentrations up to 10x MRL and ±10% for concentrations reaching from 10x MRL to the highest calibration level.[9] All duplicate analysis results are found to be well within the declared limits. The good consistency of both the initial and duplicate samples within the validation shows that this method is suitable for the analysis of drinking and natural water samples and the reproducibility of the generated results is very high. Tables 10 and 11 give an overview of the analysis results for the seven drinking and natural water samples, listing the mean value of the duplicate analysis and their RPD.

Table 10. Analysis results (mg/L) and RPD (%) of duplicate analyses of standard anions.

Analyte	Drinking Water Straubing	Drinking Water Hamlar	Mineral Water 1	Mineral Water 2
Fluoride	0.33 (-0.4)	0.13 (0.5)	0.15 (-1.6)	0.12 (-1.2)
Chloride	44.8 (0.0)	15.9 (0.1)	18.4 (0.0)	0.43 (0.6)
Nitrite	n.d.	n.d.	n.d.	n.d.
Bromide	< MRL	< MRL	< MRL	n.d.
Nitrate	23.6 (-0.8)	9.9 (0.1)	0.29 (-0.7)	< MRL
Phosphate	n.d.	n.d.	n.d.	n.d.
Sulfate	31.5 (1.1)	29.8 (0.3)	22.2 (-0.1)	10.3 (0.5)
Analyte	**Melted Snow**	**Stream Water Staltannen**	**Lake Water Hamlar**	
Fluoride	n.d.	0.07 (-1.4)	0.11 (0.2)	
Chloride	0.19 (-1.3)	1.2 (0.0)	46.1 (-0.3)	
Nitrite	n.d.	n.d.	n.d.	
Bromide	n.d.	n.d.	< MRL	
Nitrate	0.78 (0.0)	3.7 (-1.1)	0.24 (3.8)	
Phosphate	n.d.	n.d.	n.d.	
Sulfate	< MRL	1.7 (2.1)	42.2 (-1.6)	

Table 11. Analysis results (mg/L) and RPD (%) of duplicate analyses of standard cations.

Analyte	Drinking Water Straubing (Diluted 1:1)	Drinking Water Hamlar (Diluted 1:1)	Mineral Water 1	Mineral Water 2
Lithium	n.d.	n.d.	n.d.	n.d.
Sodium	35.3 (-0.3)	5.3 (2.7)	15.4 (-0.4)	8.7 (-0.6)
Ammonium	n.d.	n.d.	n.d.	n.d.
Potassium	1.9 (-7.3)	0.86 (-7.2)	1.6 (-3.2)	0.87 (-1.6)
Calcium	41.5 (0.5)	46.1 (0.7)	49.9 (0.8)	43.0 (0.1)
Magnesium	11.6 (2.0)	12.2 (1.1)	4.8 (-1.2)	21.6 (0.1)
Analyte	**Melted Snow**	**Stream Water Staltannen (Diluted 1:1)**	**Lake Water Hamlar (Diluted 1:1)**	
Lithium	n.d.	n.d.	n.d.	
Sodium	< MRL	1.0 (-3.1)	11.2 (-1.0)	
Ammonium	0.28 (1.3)	n.d.	n.d.	
Potassium	n.d.	< MRL	1.9 (-8.1)	
Calcium	n.d.	40.9 (0.7)	29.4 (1.4)	
Magnesium	n.d.	9.6 (0.7)	14.0 (-0.9)	

Initial, continuing and end calibration check standards were injected at the beginning of the sample injections, after ten injections each during the sequence and at the end of the sequence. During the validation, the 5% anion calibration standard and the 10% cation calibration standard were employed as check standards. The EPA 300.1 requirement for deviation of the check standard is ±15%.[9] During the validation, the check standards did not differ by more than 6.4% from the corresponding anion calibration standard and 8.5%

from the corresponding cation calibration standard respectively. In most cases, the difference was less than 3% for anions and less than 5% for cations. For evaluation, the peak areas of each ion in the calibration standard and the corresponding check standard were directly compared to each other.

Analyte Recovery in Fortified Water Samples

The performance of methods used for environmental analysis are typically validated by single- and multi-operator precision and bias studies on fortified samples (Laboratory Fortified Matrix, LFM). Tables 13 and 14 show the obtained recovery results for single-operator data for the standard inorganic ions spiked into drinking and natural water samples with different matrices. The samples were spiked with the standard stock solutions used for the calibration at approximately the same levels as specified in the EPA Method 300.1. The method specifies, that the samples have to be fortified ideally at the same concentrations that are found in the unfortified sample for the respective ions. However, the fortified concentration should not exceed a level five times as high as the concentration of the unfortified sample and not be less than the analyzed concentration in the unfortified sample, which implies, that recovery data of samples with analyte contents of more than 50% of the maximum calibration concentration are not collected. The minimum fortification level for analytes, that are not detected or detected below the MRL, is 5x MRL.

Additionally, a Laboratory Blank is fortified at the highest amount added to one of the LFMs for each ion respectively (Laboratory Fortified Blank, LFB). An LFB is prepared for both anions and cations each. Table 12 summarizes the recoveries found in the Laboratory Fortified Blank for both validations.

Table 12. Recovery Data of the Laboratory Fortified Blank (LFB).

Analyte	Amount added (mg/L)	Recovery (%)
Fluoride	0.5	100.1
Chloride	50	97.9
Nitrite	2	90.9
Bromide	2	91.6
Nitrate	25	97.7
Phosphate	5	79.9
Sulfate	45	102.1
Lithium	0.2	96.2
Sodium	15	108.7
Ammonium	1	76.1
Potassium	4	93.2
Calcium	5	89.0
Magnesium	15	99.7

Table 13. Recovery Data from fortified Drinking and Natural Water Samples for standard anions.

Analyte	Drinking Water Straubing		Drinking Water Hamlar		Mineral Water 1		Mineral Water 2	
	Amount added (mg/L)	Recovery (%)	Amount added (mg/L)	Recovery (%)	Amount added (mg/L)	Recovery (%)	Amount added (mg/L)	Recovery (%)
Fluoride	0.5	101.2	0.5	97.7	0.5	96.4	0.5	100.0
Chloride	45	104.2	20	102.8	20	101.2	1	83.1
Nitrite	2	87.8	2	93.3	2	91.9	2	100.6
Bromide	2	92.3	2	91.9	2	92.0	2	91.9
Nitrate	25	106.5	10	100.1	2	89.0	2	89.3
Phosphate	5	78.0	5	80.2	5	91.6	5	92.3
Sulfate	35	(111.5)*	30	(110.4)*	25	106.2	15	103.9
Analyte	**Melted Snow**		**Stream Water Staltannen**		**Lake Water Hamlar**			
	Amount added (mg/L)	**Recovery (%)**	**Amount added (mg/L)**	**Recovery (%)**	**Amount added (mg/L)**	**Recovery (%)**		
Fluoride	0.5	99.8	0.5	100.8	0.5	97.4		
Chloride	1	81.5	2	87.2	50	102.0		
Nitrite	2	99.9	2	99.8	2	86.4		
Bromide	2	91.8	2	92.3	2	91.7		
Nitrate	2	88.3	5	93.3	2	86.1		
Phosphate	5	85.4	5	85.8	5	85.8		
Sulfate	2	96.5	2	96.0	45	(108.8)*		

* Concentration of fortified sample is above the highest calibration level

Table 14. Recovery Data from fortified Drinking and Natural Water Samples for standard cations.

Analyte	**Drinking Water Straubing (Diluted 1:1)**		**Drinking Water Hamlar (Diluted 1:1)**		**Mineral Water 1**		**Mineral Water 2**	
	Amount added (mg/L)	**Recovery (%)**	**Amount added (mg/L)**	**Recovery (%)**	**Amount added (mg/L)**	**Recovery (%)**	**Amount added (mg/L)**	**Recovery (%)**
Lithium	0.2	106.2	0.2	109.3	0.2	95.0	0.2	93.4
Sodium	–	–	5	107.5	15	105.4	2	83.8
Ammonium	1	77.6	1	91.9	1	78.5	1	100.0
Potassium	4	105.2	4	89.6	4	86.7	4	80.8
Calcium	–	–	–	–	–	–	–	–
Magnesium	15	106.4	15	105.7	5	108.0	–	–
Analyte	**Melted Snow**		**Stream Water Staltannen (Diluted 1:1)**		**Lake Water Hamlar (Diluted 1:1)**			
	Amount added (mg/L)	**Recovery (%)**	**Amount added (mg/L)**	**Recovery (%)**	**Amount added (mg/L)**	**Recovery (%)**		
Lithium	0.2	99.4	0.2	93.9	0.2	94.1		
Sodium	2	105.0	2	107.2	10	101.5		
Ammonium	1	85.1	1	95.0	1	88.3		
Potassium	4	94.8	4	92.9	4	96.2		
Calcium	5	100.7	–	–	–	–		
Magnesium	5	100.4	10	109.9	15	(110.7)*		

* Concentration of fortified sample is above the highest calibration level

The specification for the recoveries given in EPA Method 300.1 is ±25% for the LFMs and LFB, and ±15% for the LFB, if the fortification level of the LFB is >10x MRL.[9] The LFB shows recovery results of 79–103% for anions, which, apart from the phosphate recovery, is within the specified range. For cations the recoveries in the LFB range from 76–109%, with ammonium being the only cation outside the specified range of ±15%. The recoveries of anions for the LFM are ranged from 78–107%, which is within the specified range. The recoveries of sulfate in the two drinking water samples and the lake water sample were determined, but should not be evaluated, since the concentrations of the fortified samples are above the highest calibration point of 50 mg/L. For cations recoveries of 77–110% are found, which is also within the range of ±25%. The content of magnesium found in the fortified lake water sample was 30.2 mg/L, which is a calculated recovery of 111%, but since this concentration is above the highest calibration point of 30 mg/L it cannot be evaluated.

Column: Sykam A07 (150 x 2.6 mm) and Sykam AGC-04 (20 x 2.6 mm)
Eluent: 4.0 mM Na_2CO_3, 25 µM NaSCN
Flow Rate: 1.0 mL/min
Inj. Vol.: 50 µL
Detection: Suppressed Conductivity, Sykam Chemical Anion Suppressor (80 rpm)

Peaks:	1. Fluoride	0.11	0.58 mg/L
	2. Chloride	46.1	92.1
	3. Nitrite	-	1.7
	4. Bromide	0.02 (< MRL)	1.9
	5. Nitrate	0.24	1.9
	6. Phosphate	-	4.3
	7. Sulfate	42.2	(86.6)

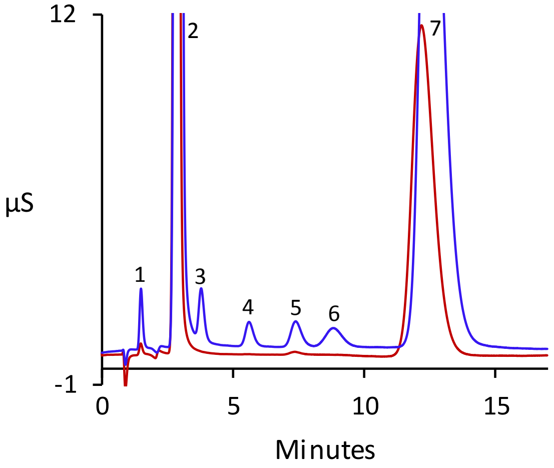

Figure 8. Determination of anions in spiked (blue) and unspiked (red) water samples of lake water.

Column: Sykam C07 (200 x 4.0 mm) and Sykam CGC-03 (50 x 4.6 mm)
Eluent: 2.0 mM Oxalic acid, 3.5 mM 2,6-Pyridine-dicarboxylic acid
Flow Rate: 1.0 mL/min
Inj. Vol.: 10 µL
Detection: Non-suppressed Conductivity

Peaks:			
	1. Lithium	-	0.19 mg/L
	2. Sodium	11.2	21.0
	3. Ammonium	-	0.88
	4. Potassium	1.9	5.7
	5. Calcium	29.4	29.8
	6. Magnesium	14.0	(30.2)

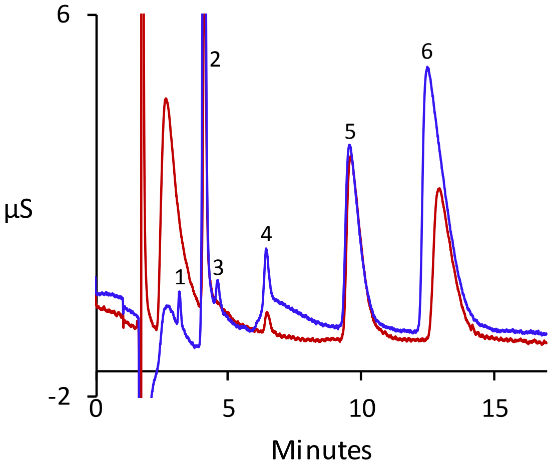

Figure 9. Determination of cations in spiked (blue) and unspiked (red) water samples of lake water.

Summary

The Sykam A07 and C07 columns provide suitable performance for the simultaneous determination of inorganic anions and cations including ammonium in natural and drinking waters, as outlined in U.S. EPA Method 300.1, ASTM D4327 and ISO EN 10304-1 for anions and ASTM D6919 for cations. This was shown by a full method validation with respect to all specifications given in the mentioned guidelines concerning the determination of method detection limits, resolution, linearity and precision. Good recovery data for the fortified sample matrices as well as for the fortified blank were found under the described chromatographic conditions. The Sykam A07 exhibits a high capacity, as the linearity range was determined over more than two orders of magnitude, making it possible to analyze samples of up to 100 mg/L of chloride or other inorganic anions without a time-consuming dilution step. The Sykam A07 as well as the Sykam C07 reveals a high resolution for all examined standard ions, making these columns suitable for the analyses of complex matrices or large concentration differences between closely eluting peak pairs.

References

[1] *Official Journal of the European Communities*: Council Directive 98/83/EC of 3 November 1998 on the quality of water intended for human consumption.

[2] *Official Journal of the European Union*: Directive (EU) 2020/2184 of the European Parliament and of the Council of 16th December 2020 on the quality of water intended for human consumption (recast).

[3] Safe Drinking Water Act (Title XIV of the Public Health Service Act, Chapter 373 of the 78th Congress).

[4] *Official Journal of the European Communities*: Directive 2000/60/EC of the European Parliament and of the Council of 23 October 2000 establishing a framework for Community action in the field of water policy.

[5] U.S. Clean Water Act (33 U.S.C. §1251 et seq. (1972))

[6] www.epa.gov/ground-water-and-drinking-water/national-primary-drinking-water-regulations (accessed January 18, 2023).

[7] R.V. Thurston, R.C. Russo, *Environ. Sci. Technol.* **1981**, *15 (7)*, 837–840.

[8] EN ISO 10304-1:2009: Water quality – Determination of dissolved anions by liquid chromatography of ions – Part 1: Determination of bromide, chloride, fluoride, nitrate, nitrite, phosphate and sulfate.

[9] Method 300.1 – Determination of Inorganic Anions in Drinking Water by Ion Chromatography, Revision 1.0, National Exposure Research Laboratory, Office of Research and Development, U.S. Environmental Protection Agency, Cincinnati, OHIO 45268.

[10] ASTM International: Designation D4327-17, Standard Test Method for Anions in Water by Suppressed Ion Chromatography.

[11] ASTM International: Designation D6919-17, Standard Test Method for Determination of Dissolved Alkali and Alkaline Earth Cations and Ammonium in Water and Wastewater by Ion Chromatography.

[12] EN ISO 14911:1999: 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

[13] 40 CFR Appendix -B-to-Part-136 – Definition and Procedure for the Determination of the Method Detection Limit – Revision 2.

[14] DIN 38402-51 – German standard methods for the examination of water, waste water and sludge – General information (group A) – Part 51: Calibration of analytical methods – Linear calibration (A 51).

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