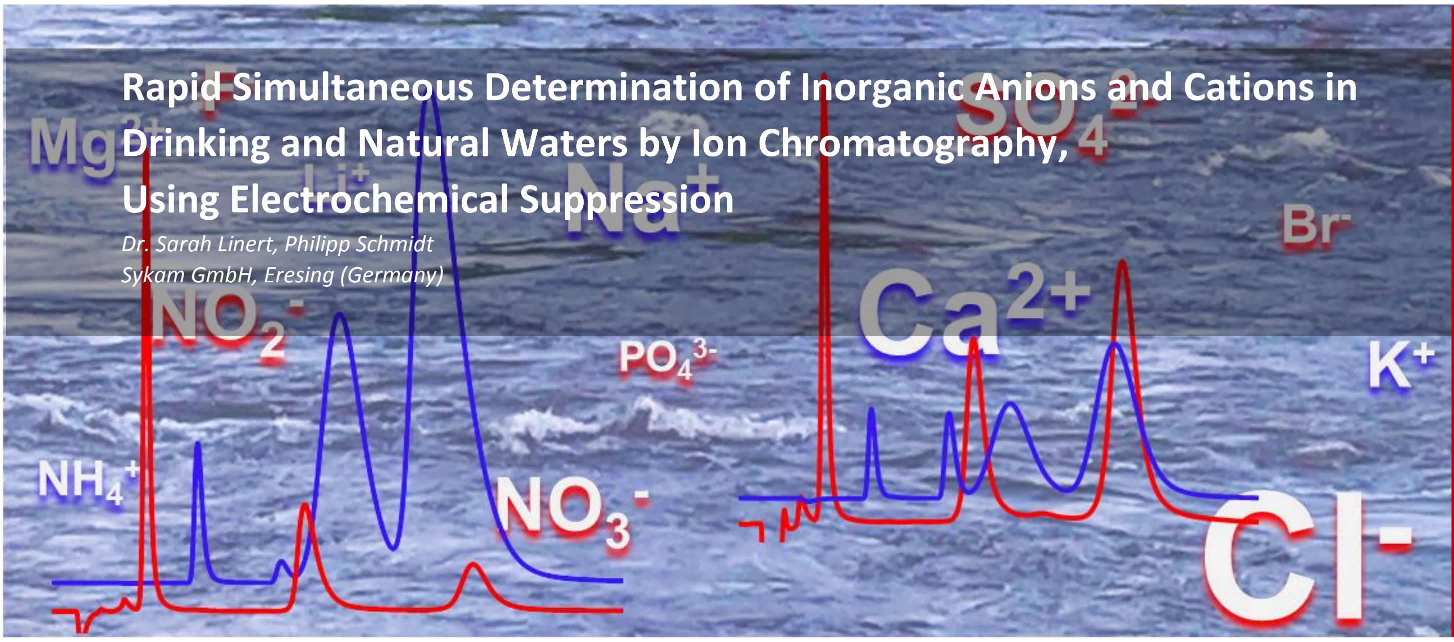

Rapid Simultaneous Determination of Inorganic Anions and Cations in Drinking and Natural Waters by Ion Chromatography, Using Electrochemical Suppression

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Sykam Application Note 10

Introduction

The impact humans have on the planet is ever growing. Whether climate change or pollution, the consequences for the environment, caused by continuing industrial growth, are undeniable. With an increasing population, the need to monitor our negative influence on the planet grows, both for environmental protection and to prevent possible health hazards. As one of our most precious resources, drinking water requires special attention. Therefore, many countries around the globe have implemented regulations to ensure the quality of water, both to protect the ecosystem and the population. Amongst these are the European Union's Drinking Water Directive (DWD) 98/83[1] (1998, latest version 2020/2184 from December 2020)[2] and the Safe Drinking Water Act (SDWA) established in the United States in 1974,[3] both of which aim to secure the quality of drinking water for human consumption. Likewise, the Water Framework Directive (2000/60/EC) of the European Union, attempts to preserve surface, transitional, coastal and groundwaters in order to maintain and enhance the status of aquatic ecosystems,[4] while in the United States, the Clean Water Act (CWA) aims to reduce the amount of pollutants released into the environment.[5]

These pollutants are sorted into primary and secondary contaminants and are regulated in the U.S. National Primary and Secondary Drinking Water Standard (NPDWS/NSDWS)[6] and the EU DWD.[2] In the United States, fluoride, nitrite and nitrate are considered primary contaminants and are regulated by the NPDWS, while chloride and sulfate are categorized as secondary contaminants and covered by the NSDWS accordingly.[6] In the European Union, these inorganic ions are also regulated by the Drinking Water Directive.[2] Additionally, the common cations present in drinking water are also regulated, and reported by most suppliers in the European Union, in contrast to the United States, where they are not considered primary contaminants.[2,6] In the European Union, magnesium and calcium are also measured, to determine the hardness of water. Similarly to the United States and the European Union, other parts of the world have passed their own regulations to protect and monitor drinking and natural waters, some of which are based on the aforementioned regulations.

Many national and international standard organizations have defined regulations and methods for the analysis of drinking and natural waters. Amongst them the International Organization for Standardization (ISO), the American Society for Testing and Materials (ASTM), the American Water Works Association (AWWA) and the United States Environmental Protection Agency (EPA). The primary analytical technique, defined by these organizations for monitoring the quantity of ionic species in drinking and natural waters, is Ion Chromatography (IC). As such, a number of regulatory IC methods for the analysis of anions in drinking and natural waters have been published worldwide, including the EN ISO 10304-1[7] (Technical Committee ISO/TC 147 "Water quality"), the EPA 300.1[8] or the ASTM D4327.[9] Likewise, the methods for analysis of cations using IC are described in ASTM D6919[10] and EN ISO 14911.[11] These allow the use of IC for the determination of alkaline and alkaline earth metals alongside ammonium in a single run.

These methods define quality control parameters and measuring conditions, but also state that optional columns and corresponding, different chromatographic conditions may be used to improve the separations or lower the costs of measurement.[7-9] A major factor of measurement cost, is the run time of a method. With a growing population and industry around the world, more and more samples need to be measured to ensure the continued quality of drinking and natural waters. Shorter run times not only allow more samples to be measured faster, but also consume less reagents and electricity to do so and reduce the stress put on analytical equipment, such as columns, increasing their lifespan.

The method described in this application note "Sykam AN10" was developed precisely to fulfill the need for fast, yet reliable analysis of drinking and natural waters. It describes the rapid, simultaneous determination of inorganic anions and cations in water samples by IC using suppressed conductivity measurement. 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[8], EN ISO 10304-1:2009-07[7] and ASTM D4327-17[9] as well as ASTM D6919[10] and EN ISO 14911[11] using a Sykam S153+ Dual IC module. The columns Sykam A09 (75 x 2.6 mm) and Sykam C08 (250 x 2.6 mm) were used for the method validation and the validation results are discussed within this application note.

Equipment

Application note “Sykam AN10” is designed for the use of a Sykam S153-AG Dual+ IC system with dual-channel anion and cation conductivity detection using electrochemical suppression, consisting of the following components:

- S150+ Ion Chromatography Module including column oven, two-channel conductivity detectors and electrochemical anion and cation self-regenerating suppressor modules
- 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 or 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)
- Methanesulfonic acid (CH_4SO_3, ≥99.0%), Sigma-Aldrich (1003354630)
- 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)
- 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)
- 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)

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 preferred for the 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)
- Magnesium nitrate hexahydrate ($Mg(NO_3)_2 \cdot 6\ H_2O$, ACS reagent, 99%), Sigma-Aldrich (237175)
- Calcium nitrate tetrahydrate ($Ca(NO_3)_2 \cdot 4\ H_2O$, for analysis EMSURE, ACS, ISO, Reag. Ph Eur), Merck (1.02121)

Samples

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

Table 1. List of analyzed samples.

No.	Name
1	Drinking Water (Karsfeld)
2	Drinking Water (Pitzling)
3	Mineral Water 1
4	Mineral Water 2
5	Lake Water (Karlsfelder See)
6	River Water (Würm)

All six water samples were collected in southern Germany in the northern foothills of the Alps, where lime containing soil is the predominant geological formation. The drinking water samples were collected as tap water from two different municipal water suppliers in Karlsfeld and Pitzling. The mineral water samples were commercially available mineral waters from companies, that obtain their water from natural groundwater sources. The lake water was collected from the Karlsfeld Lake and the river water was collected from the river Würm near Allach-Untermenzing in Munich. All samples were collected in 1000 mL PE-bottles with a screw cap and stored at 4 °C immediately after collection.

Chromatographic Conditions

Method Validation Anions

Columns:	Sykam A09 (75 x 2.6 mm), Analytical Column Sykam AGC-05 (20 x 2.6 mm), Guard Column
Eluent:	3.5 mM Na_2CO_3, 25 µM NaSCN
Flow Rate:	1.2 mL/min
Run Time:	9 min
Temperature:	35 °C
Injection Volume:	50 µL (full loop)
Detection:	Suppressed Conductivity, Electrochemical Self-Regenerating Anion Suppressor
Suppressor Current:	40 mA
Backpressure:	148 bar (2147 psi)
Base Conductivity:	17 µS/cm
Noise:	<3 nS/cm

Method Validation Cations

Columns:	Sykam C08 (250 x 2.6 mm), Analytical Column Sykam CGC-04 (20 x 2.6 mm), Guard Column
Eluent:	7.5 mM Methanesulfonic acid
Flow Rate:	1.0 mL/min
Run Time:	9 min
Temperature:	35 °C
Injection Volume:	10 µL (full loop)
Detection:	Suppressed Conductivity, Electrochemical Self-Regenerating Cation Suppressor
Suppressor Current:	35 mA
Backpressure:	121 bar (1755 psi)
Base Conductivity:	0.4 µS/cm
Noise:	<1 nS/cm

All settings listed here are part of the chromatographic method and can be saved in the "Method Setup" window of the Clarity software. To achieve reproducible results, only full loop injections were performed. During the dual analysis, both injection loops are connected in series, meaning that an injection volume of at least 100 µL needs to be programmed in the sequence to fill both loops with at least 50% excess.

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 be 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
Magnesium	Magnesium nitrate hexahydrate ($Mg(NO_3)_2 \cdot 6\ H_2O$)	10.547
Calcium	Calcium nitrate tetrahydrate ($Ca(NO_3)_2 \cdot 4\ H_2O$)	5.892

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 anion and cation standards at concentrations of 200, 100, 50, 20, 10, 5, 2 and 1 µg/L of each ion are prepared from 10 mg/L single standard solutions for the preliminary estimation of the method detection limit.

As mentioned in ASTM D6919[10] and EN ISO 14911,[11] a low pH value of the sample can interfere with analysis, resulting in peak splitting of the alkaline earth metals at high concentrations. As most of the commercially available cation standard stock solutions are solutions of the corresponding salts in 0.5 mol/L HNO_3, these solutions are acidic with a pH of approximately 1. Therefore, the standard stock solutions used for cation analysis were prepared from the corresponding salts as described above, while commercially available standard stock solutions were used for anion analysis.

Table 3 lists 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 system.

The determination of the linear calibration range of the seven standard anions, and the six standard cations, covering the expected concentrations of the drinking and natural water samples, is achieved by injecting twelve levels of calibration of a mixed anion and cation standard at the following concentrations: 0.05, 0.1, 0.2, 0.5, 1.0, 2.0, 5.0, 10, 20, 50, 75 and 100 mg/L (0.02–20 mg/L for fluoride and lithium). All concentration levels are prepared from the 1000 mg/L standard stock solutions.

Table 3. Concentrations of MDL_S calculation, QCS and 100% linearity standard.

Analyte	MDL_S Calculation Standard Anions (µg/L)	QCS for Precision Anions (mg/L)	Maximum Standard Concentration Anions (mg/L)
Fluoride	10	2	20
Chloride	5	10	100
Nitrite	40	2	100
Bromide	60	2	100
Nitrate	60	20	100
Phosphate	200	2	100
Sulfate	80	30	100
Analyte	**MDL_S Calculation Standard Cations (µg/L)**	**QCS for Precision Cations (mg/L)**	**Maximum Standard Concentration Cations (mg/L)**
Lithium	5	2	20
Sodium	5	15	100
Ammonium	20	5	100
Potassium	5	10	100
Magnesium	20	20	100
Calcium	30	40	100

To assess the performance of the chromatographic system, External Control Samples (ECS) are prepared at the same concentrations as the QCS (Table 3). In the case of the anions, self-prepared 1000 mg/L stock solutions (salt amounts according to Table 2) are used, whereas commercially available 1000 mg/L stock solutions are used for the cations.

Eluent solutions

The eluents for anion analysis 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, when 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 chromatographic system discussed here, the following eluents are prepared:

Anions (Sykam A09): 3.5 mM Na_2CO_3, 25 µM NaSCN – 7.0 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 pressurized with inert gas (optional).

Cations (Sykam C08): 7.5 mM methanesulfonic acid – 974.4 µL methanesulfonic acid are added to 2000 mL of deionized water. The solution is mixed thoroughly and then filtered over a 0.45 µm regenerated cellulose filter disc. The eluent is transferred to the S7150 Reagent Organizer and the container is pressurized 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 1.2 mL/min (A09) and 1.0 mL/min (C08). To achieve reproducible results, the system, and especially the suppressor units, have to warm up and be equilibrated. For equilibration, switch on the column oven and the suppressors at the respective conditions. Apply the desired flow rate until the baseline has stabilized. The baseline noise should be no higher than 5.0 nS/cm for either channel. If the system has not been in use for several days or longer, it should be equilibrated for 3 hours. For a faster equilibration, a higher suppressor current (150 mA) can be applied for 2 hours at the desired flow rate of 1.2 mL/min or 1.0 mL/min respectively. If the system is used on a daily basis, the column oven, as well as the suppressor unit, should be left switched on overnight, at a low flow rate (0.1 mL/min) and a suppressor current of 5 mA, so that the system can readily be used for the following analyses. In this case, the suppressor current should be reduced to 5 mA 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, mineral 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 identically 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, which might lead to a change of 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),[8] as well as ISO EN 10304-1:2009-07[7] and ASTM D4327-17[9] ensuring that all requirements of these methods regarding quality control parameters are met. As mentioned above, the methods define that optional columns and corresponding, different chromatographic conditions may be used, to improve separation or lower the cost of measurement. Here, the Sykam A09 column, together with the Sykam S153-AG+ Dual IC system under the chromatographic conditions listed above were used for the validation. All required quality control parameters were tested including:

- Determination of Method Detection Limits MDL$_S$ and MDL$_B$[12]
- Linearity (Linear Calibration Range, LCR)[13]
- Precision, by repeated injection of a Quality Control Sample (QCS)
- Accuracy of 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 duplicates
- Assessment of analyte recovery by injection of Laboratory Fortified Matrices (LFM) for each sample

Additionally, instrument performance was checked throughout the entire sequence by analysis of initial, continuing and end calibration check standards.

The Sykam A09 is an anion exchange column optimized for rapid analysis of the standard anions. Its substrate is based on trimethylammonium functionalized PS-DVB with a particle size of 5 µm. Figure 1 shows the separation of an inorganic anion calibration standard using the Sykam A09.

Likewise, the method validation for the determination of cations in drinking and natural waters was performed according to the regulations listed in ASTM D6919[10] and EN ISO 14911,[11] using the Sykam C08 column under the chromatographic conditions listed above. The same quality control parameters were tested as for the anion method validation.

Column: Sykam A09 (75 x 2.6 mm) and Sykam AGC-05 (20 x 2.6 mm)
Eluent: 3.5 mM Na_2CO_3, 25 µM NaSCN
Flow Rate: 1.2 mL/min
Inj. Vol.: 50 µL
Detection: Suppressed Conductivity, Electrochemical Self-Regenerating Anion Suppressor (40 mA)

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

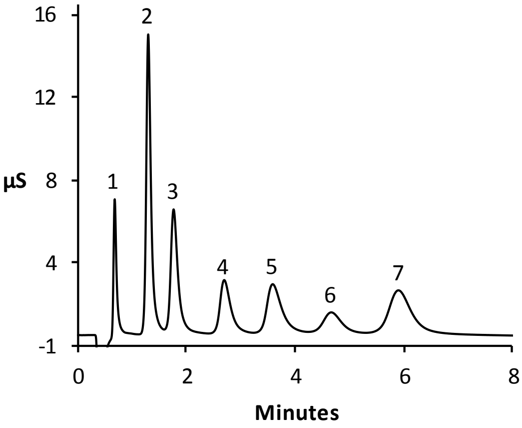

Figure 1. Separation of the 5% calibration standard for inorganic anions.

Table 4. Column performance parameters of Sykam A09 (5% calibration standard) and Sykam C08 (5% calibration standard) at the chromatographic conditions listed above.

Analyte	Retention time (min)	Resolution R	Peak Symmetry
Fluoride	0.68	–	1.95
Chloride	1.29	4.91	1.42
Nitrite	1.76	2.47	1.49
Bromide	2.69	3.25	1.47
Nitrate	3.59	2.17	1.49
Phosphate	4.67	2.03	1.18
Sulfate	5.91	1.89	1.35
Lithium	1.69	–	1.58
Sodium	2.03	1.68	1.61
Ammonium	2.41	1.45	1.38
Potassium	3.22	2.60	1.79
Magnesium	4.19	1.31	1.24
Calcium	5.83	1.36	1.25

The Sykam C08 is a weak cation exchange column based on a 9 µm particle size EVB-DVB resin, functionalized with weak carboxylic acids. Figure 2 shows the separation of an inorganic cation calibration standard using the Sykam C08.

The peak resolution is R >1.3 for all standard anions and cations (Table 4), as required by EN ISO 10304-1[7] and EN ISO 14911.[11] The columns exhibit good peak symmetry, allowing exact integration of peak areas.

Column: Sykam C08 (250 x 2.6 mm) and Sykam CGC-04 (20 x 2.6 mm)
Eluent: 7.5 mM Methanesulfonic acid
Flow Rate: 1.0 mL/min
Inj. Vol.: 10 µL
Detection: Suppressed Conductivity, Electrochemical Self-Regenerating Cation Suppressor (35 mA)

Peaks:		
	1. Lithium	1.0 mg/L
	2. Sodium	5.0
	3. Ammonium	5.0
	4. Potassium	5.0
	5. Magnesium	5.0
	6. Calcium	5.0

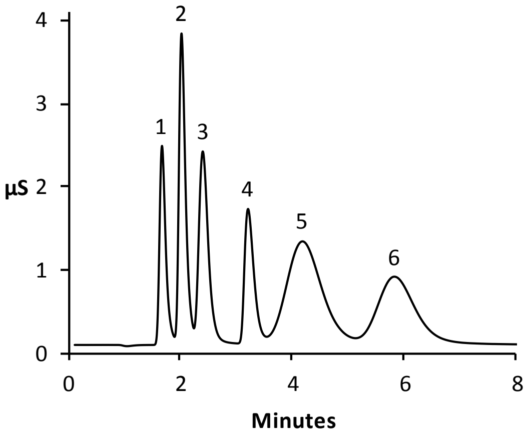

Figure 2. Separation of the 5% calibration standard for inorganic cations.

Method Detection Limits MDL_S and MDL_B

First the method detection limits based on sample injections (MDL_S) were estimated. Therefore, six mixed anion standards with the following concentrations were injected: 200, 100, 50, 20, 10, 5, 2 and 1 µg/L of each anion. The same procedure was used to determine the MDL_S of the cations, using the same concentrations. 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 $MDL_S = t \times SD$, 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 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 no anions and cations, besides sodium were found. Sodium was detected at a mean level of 75.6 µg/L. Therefore, for sodium, the method detection limit MDL_S does not apply and the MDL_B is calculated instead: $MDL_B = X + t \times SD$, where X is the mean of the LRB results.[11] 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 sodium was calculated as 0.12 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 therefore recommend the use of a S150+ IC system in single-channel cation detection mode with an electrochemical self-regenerating cation suppressor.

Linearity (LCR)

To assess the linear calibration range for each ion, mixed standards at twelve calibration levels were injected for anions and cations respectively: 0.05 0.1, 0.2, 0.5, 1.0, 2.0, 5.0, 10, 20, 50, 75 and 100%. The anion standard contained 100 mg/L of all standard anions aside from fluoride, which had a concentration of 20 mg/L. Likewise, the cation standard contained all standard cations at a concentration of 100 mg/L aside from lithium, which was contained at 20 mg/L. 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 within a linear range, were used to assess the calibration curve individually for each ion. Figure 3 shows the calibration plots for all ions. Calibration points that are outside the linear range were omitted and are displayed in red. For fluoride and lithium, a calibration range of 0.01–20 mg/L was determined, which is sufficiently high, as both of these ions are usually only contained in trace amounts (<1.0 mg/L) in natural water samples. Nitrite, which is also rare in high concentrations in natural water samples, was likewise only calibrated from 0.05–5 mg/L. All other anions exhibit a linear calibration range of 0.05–20 mg/L. Ammonium, was calibrated in a range of 0.05–20 mg/L, whereas all other cations show linear behavior in a range of 0.05–100 mg/L. For sodium, the two lowest calibration points (0.05 and 0.1 mg/L) where omitted, as they are below the MDL_B. It should be noted that ammonium was calibrated using a quadratic fit, in accordance with EN ISO 14911[12] and D6919[11] for the calibration of ammonium using suppressed conductivity. In Tables 5 and 6 the calibration ranges, as well as the correlation factors r^2 of the linear (and quadratic) fits for all ions are listed. All 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	0.01 – 20	0.9998	1.1	0.84	1.43
Chloride	0.05 – 20	0.9998	3.0	0.42	1.57
Nitrite	0.05 – 5	0.9998	5.4	0.33	1.95
Bromide	0.05 – 20	0.9998	2.9	0.26	1.46
Nitrate	0.05 – 20	0.9997	12.3	0.27	1.78
Phosphate	0.05 – 20	0.9996	24.8	0.18	1.55
Sulfate	0.05 – 20	0.9995	23.6	0.16	1.54

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	0.01– 2	1.0000	0.3	0.35	0.19
Sodium	0.2 – 100	1.0000	1.1*	0.28	0.18
Ammonium	0.05 – 20	0.9995	2.5	0.23	0.18
Potassium	0.05 – 100	1.0000	0.5	0.18	0.25
Magnesium	0.05 – 100	1.0000	2.4	0.14	0.13
Calcium	0.05 – 100	1.0000	4.1	0.10	0.17

* Value not valid, MDL_B is used instead

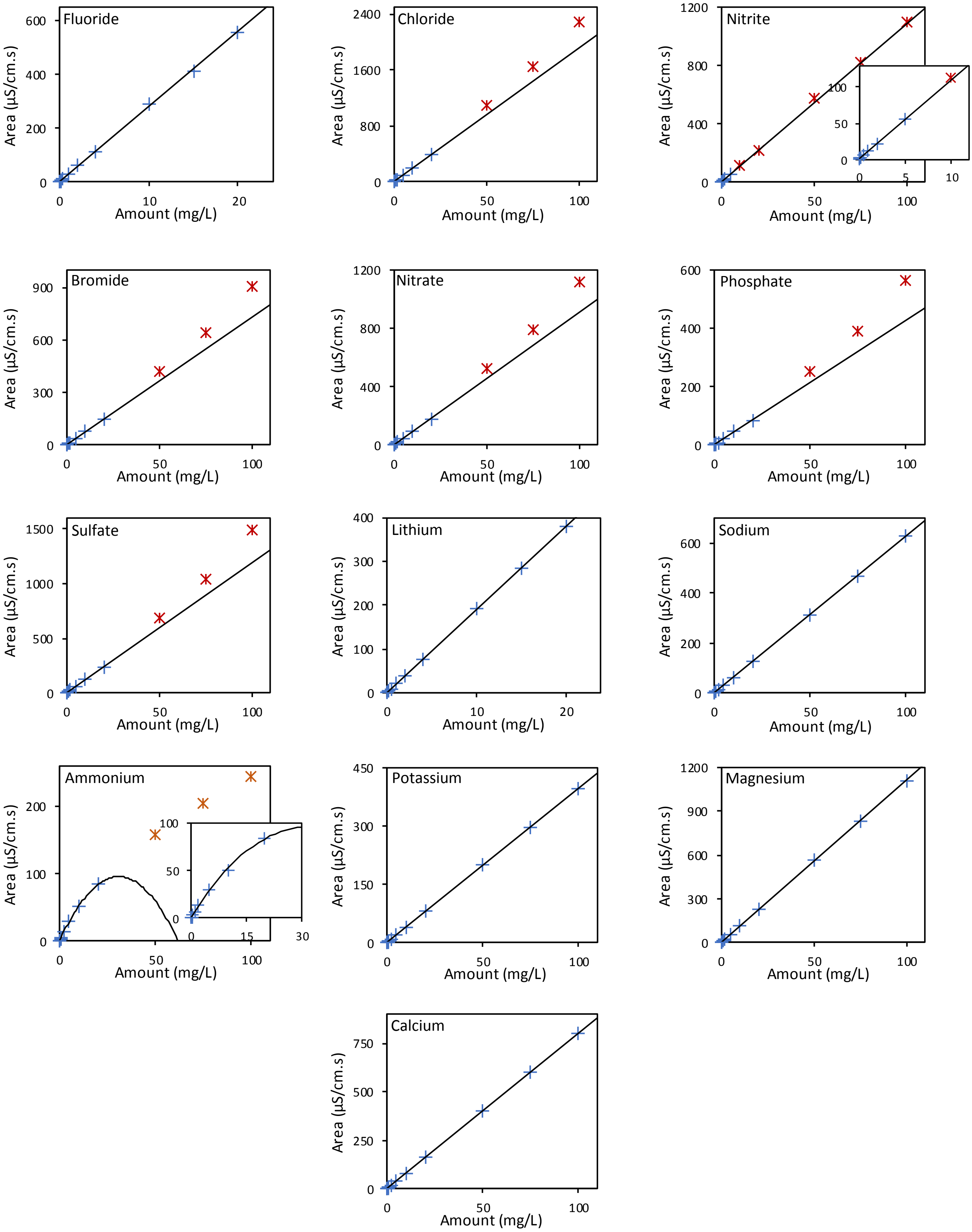

Figure 3. Calibration plots of the standard anions and cations indicating the LCR used for analysis of the samples.

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

Analyte	RPD (%)
Fluoride	0.0
Chloride	-2.3
Nitrite	2.1
Bromide	-2.6
Nitrate	-1.7
Phosphate	-3.1
Sulfate	-0.7
Lithium	1.8
Sodium	-1.1
Ammonium	0.7
Potassium	3.2
Magnesium	3.1
Calcium	-3.4

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 of seven replicate injections of the QCS. For all investigated ions, the RSDs of the retention times are well below 1.0% as are the RSDs of the peak areas for the cations. For the anions, all peak area RSDs are below 2.0%, as required. These values illustrate the high precision achieved with the Sykam S153-AG Dual+ IC system using the Sykam A09 and Sykam C08 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 instrument performance was verified by the analysis of an External Calibration Standard (ECS). The ECS is prepared from 1000 mg/L single ion 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, which were used for the preparation of the calibration standards. Therefore, for the anions, the QCS was prepared from commercially available standard stock solutions and the ECS was prepared from self-prepared stock solutions and vice versa for the cation QCS and ECS. If used for verification of instrument performance, the acceptance range for the Relative Percent Differences (RPD) between the ECS and the QCS is ±15%.[8] In Table 7 the RPDs of the ECS and the QCS are listed. The determined differences are well within the specified deviation range of ±15%.[8]

Sample Analysis

All six samples (Table 1) were analyzed twice after filtration, as initial sample and laboratory duplicate. If the measured concentration of a sample exceeded the calibration range, it was diluted, to ensure the ion with the highest concentration was within the calibration range. Values recorded from a diluted sample were multiplied by the dilution factor in the report, to reflect the sample's original concentration. If the concentration of an ion was below the determined Minimum Reporting Level (MRL) its value was not recorded, as the accuracy of the measurement cannot be guaranteed. Likewise, if the concentration of an ion fell below the MRL during dilution, the value of the undiluted sample is reported to ensure linear behavior. 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.[8] Table 8 gives an overview of the MRLs for each ion based on the applied linear calibration ranges and calculated MDLs.

For the anions (Table 10), nitrite was detected in all samples, except mineral water 2, at very low concentrations bellow the MRL, while bromide was only detected in the drinking and mineral water samples at similarly low concentrations. Low concentrations of fluoride were found in all samples, ranging from 0.06 to 0.83 mg/L. Chloride and nitrate were also detected in all samples with a wide range of concentrations ranging from 0.95 mg/L in mineral water 2 to 48.3 mg/L in the lake water for chloride and from only 0.13 mg/L in mineral water 1 to 26.9 mg/L in drinking water 2 for nitrate. With concentrations of 10.1 all the way up to 67.7 mg/L in mineral water 2, sulfate was the anion with the highest concentrations overall, while phosphate was only detected in 3 samples, including the river water sample. Here the concentration was below the MRL and phosphate could no longer be detected after dilution.

For the cations (Table 11), lithium was detected at values below the MRL in all water samples, while ammonium could not be detected in any. Potassium was detected in all samples at low concentrations of 0.93 to 3.22 mg/L and magnesium at higher levels of 2.37 to 31.8 mg/L in drinking water 2. Sodium was found at a wide range of concentrations from only 0.77 mg/L in mineral water 2 to 102 mg/L in drinking water 1. With 5.89 mg/L in mineral water 2 to 106 mg/L in mineral water 1 calcium had the highest levels out of all the cations.

Table 9 summarizes the results found for mineral waters 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, with a deviation ranging from 3.1 to -13%, except for sulfate, which shows a larger variation of 19.4%. For mineral water 2, the deviance is larger, with a range of -8.0 to 17.1% for most anions and cations, with the exception of sodium at -35.3 and sulfate at 34.3%. Certain deviations between the values printed by the supplier and the measured values are to be expected, as the ion concentrations of the water sources may vary over time. Additionally, the higher deviations for mineral water sample 2, can be explained by its overall low ion concentrations, which result in even small differences in concentration leading to high deviation values.

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

Analyte	MRL (mg/L)
Fluoride	0.01
Chloride	0.05
Nitrite	0.05
Bromide	0.05
Nitrate	0.05
Phosphate	0.05
Sulfate	0.05
Lithium	0.01
Sodium	0.20
Ammonium	0.05
Potassium	0.05
Magnesium	0.05
Calcium	0.05

Column: Sykam A09 (75 x 2.6 mm) and Sykam AGC-05 (20 x 2.6 mm)
Eluent: 3.5 mM Na_2CO_3, 25 µM NaSCN
Flow Rate: 1.2 mL/min
Inj. Vol.: 50 µL
Detection: Suppressed Conductivity, Electrochemical Self-Regenerating Anion Suppressor (40 mA)

Peaks:	
1. Fluoride	0.07 mg/L
3. Chloride	16.0
4. Nitrite	0.02 (<MRL)
5. Bromide	0.01 (<MRL)
6. Nitrate	26.9
7. Sulfate	12.4

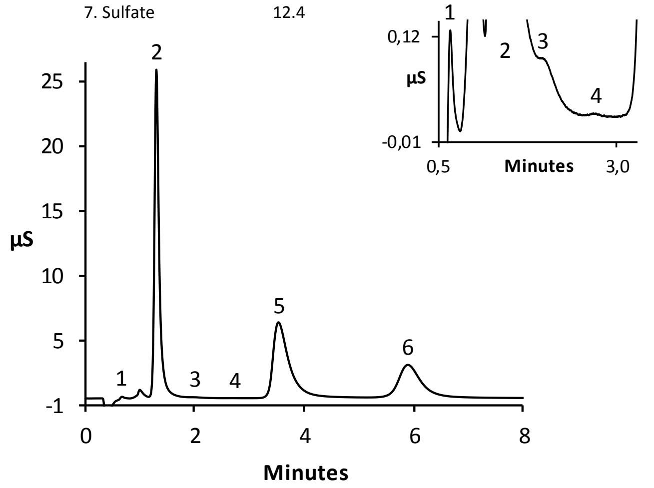

Figure 4. Determination of anions in drinking water (Pitzling), with a dilution ratio of 1:1.

Column: Sykam C08 (250 x 2.6 mm) and Sykam CGC-04 (20 x 2.6 mm)
Eluent: 7.5 mM Methanesulfonic acid
Flow Rate: 1.0 mL/min
Inj. Vol.: 10 µL
Detection: Suppressed Conductivity, Electrochemical Self-Regenerating Cation Suppressor (35 mA)

Peaks:	
1. Lithium	0.001 mg/L (<MRL)
2. Sodium	6.1
3. Potassium	1.9
4. Magnesium	31.8
5. Calcium	97.3

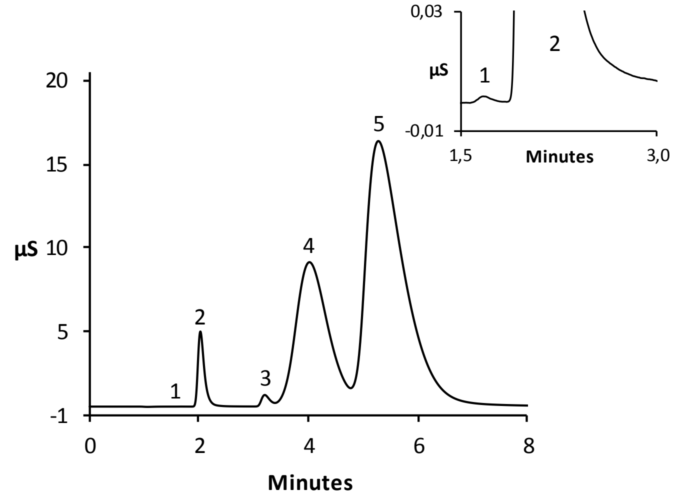

Figure 5. Determination of cations in drinking water (Pitzling), without dilution.

Column: Sykam A09 (75 x 2.6 mm) and Sykam AGC-05 (20 x 2.6 mm)
Eluent: 3.5 mM Na_2CO_3, 25 µM NaSCN
Flow Rate: 1.2 mL/min
Inj. Vol.: 50 µL
Detection: Suppressed Conductivity, Electrochemical Self-Regenerating Anion Suppressor (40 mA)

Peaks:	
1. Fluoride	0.09 mg/L
2. Chloride	48.3
3. Nitrite	0.03 (<MRL)
4. Nitrate	11.6
5. Sulfate	16.7

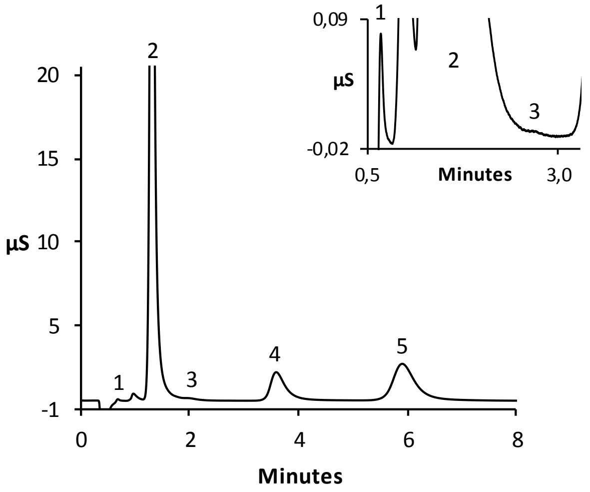

Figure 6. Determination of anions in lake water (Karlsfelder See), with a dilution ratio of 1:2.

Column: Sykam C08 (250 x 2.6 mm) and Sykam CGC-04 (20 x 2.6 mm)
Eluent: 7.5 mM Methanesulfonic acid
Flow Rate: 1.0 mL/min
Inj. Vol.: 10 µL
Detection: Suppressed Conductivity, Electrochemical Self-Regenerating Cation Suppressor (35 mA)

Peaks:	
1. Lithium	0.001 mg/L (<MRL)
2. Sodium	26.7
3. Potassium	3.2
4. Magnesium	20.6
5. Calcium	79.9

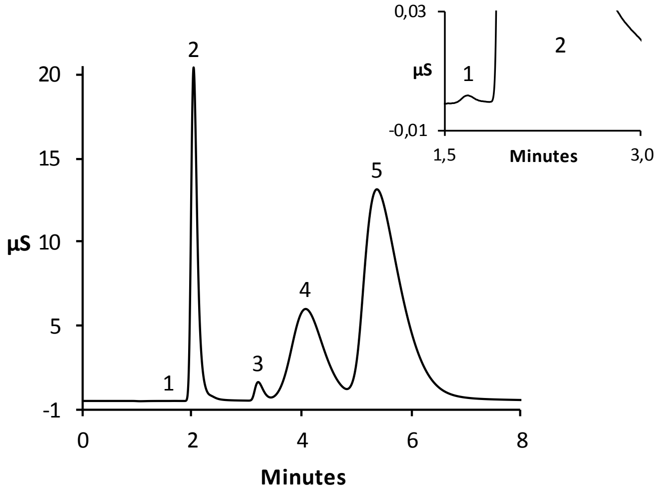

Figure 7. Determination of cations in lake water (Karlsfelder See), without dilution.

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	0.94	1.0	0.4	-
Chloride	4.0	4.3	0.95	0.8
Sulfate	68.0	56.0	4.1	2.9
Sodium	3.3	3.2	0.77	1.1
Potassium	1.5	1.6	1.5	1.7
Magnesium	3.6	4.1	2.4	2.6
Calcium	106.0	100.0	5.9	6.7

For all water samples a laboratory duplicate was measured to ensure the reproducibility of the measurements. The values found in these 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.[8] All duplicate analysis results are found to be well within the declared limits, especially for the anions, that do not exceed 5%. 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. Mean analysis results (mg/L) and RPD (%) of duplicate analyses of standard anions. The dilution ratio (if applicable) is shown in brackets.

Analyte	Drinking Water Karlsfeld	Drinking Water Pitzling (1:1)	Mineral Water 1 (1:3)
Fluoride	0.83 (0.1)	0.07 (-1.5)	0.94 (0.2)
Chloride	2.1 (1.2)	16.0 (0.0)	4.0 (0.7)
Nitrite	<MRL	<MRL	<MRL
Bromide	<MRL	<MRL	<MRL
Nitrate	0.74 (2.0)	26.9 (-0.1)	0.13 (0.8)*
Phosphate	0.092 (-3.3)	n.d.	n.d.
Sulfate	17.8(-0.1)	31.4 (-1.2)	68.0 (0.8)
Analyte	**Mineral Water 2**	**Lake Water Karlsfelder See (1:2)**	**River Water Würm (1:1)**
Fluoride	0.04 (-2.8)	0.09 (1.1)	0.07 (2.9)
Chloride	0.95 (0.5)	48.3 (0.2)	21.3 (-0.9)
Nitrite	n.d.	<MRL	<MRL
Bromide	<MRL	n.d.	n.d.
Nitrate	2.5 (0.2)	11.6 (0.3)	3.8 (-3.1)
Phosphate	0.08 (-1.2)	n.d.	<MRL**
Sulfate	4.1 (-0.1)	16.7 (0.0)	10.1 (-0.7)

* Concentration in undiluted sample, ** Anion no longer detected after dilution

Table 11. Mean analysis results (mg/L) and RPD (%) of duplicate analyses of standard cations. The dilution ratio (if applicable) is shown in brackets

Analyte	Drinking Water Karlsfeld (1:1)	Drinking Water Pitzling	Mineral Water 1 (1:3)
Lithium	0.01 (9.5)*	<MRL	<MRL
Sodium	102.4 (-0.2)	6.1 (-0.1)	3.3 (-1.0)
Ammonium	n.d.	n.d.	n.d.
Potassium	0.84 (-8.3)	1.9 (8.2)	1.5 (-0.8)
Magnesium	6.3 (-0.5)	31.8 (-0.2)	3.6 (-1.0)
Calcium	9.8 (-0.7)	97.3 (-0.4)	106.0 (0.5)
Analyte	**Mineral Water 2**	**Lake Water Karlsfelder See**	**River Water Würm**
Lithium	<MRL	<MRL	<MRL
Sodium	0.8 (2.7)	12.1 (-0.1)	12.1 (-0.1)
Ammonium	n.d.	n.d.	<MRL
Potassium	1.5 (6.4)	3.2 (1.6)	2.1 (1.3)
Magnesium	2.4 (-0.1)	20.6 (-0.3)	15.1 (-0.1)
Calcium	5.9 (-0.2)	76.9 (-0.5)	42.5 (-0.1)

* Concentration in undiluted sample

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 5% cation calibration standard were employed as check standards. The EPA 300.1 requirement for deviation of the check standard is ±15%.[8] During the validation, the check standards did not differ by more than 4.7% from the corresponding anion calibration standard and 6.4% from the corresponding cation calibration standard respectively. 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.[8] The method specifies that the samples should be fortified, ideally at the same concentrations that are found in the unfortified sample for the respective ions. Additionally, 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. If a diluted sample was used during the initial sample analysis, a diluted sample, with the same dilution factor, was used for the preparation of the LFMs.

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	1	102.1
Chloride	9	102.4
Nitrite	2	88.3
Bromide	1	96.0
Nitrate	4	101.7
Phosphate	5	101.2
Sulfate	7	106.2
Lithium	0.1	92.0
Sodium	27	98.3
Ammonium	2	111.9
Potassium	4	97.3
Magnesium	32	99.9
Calcium	43	95.4

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

Analyte	Drinking Water Karlsfeld		Drinking Water Pitzling		Mineral Water 1	
	Amount added (mg/L)	Recovery (%)	Amount added (mg/L)	Recovery (%)	Amount added (mg/L)	Recovery (%)
Fluoride	1	96.0	0.2	93.5	0.5	94.1
Chloride	3	101.4	9	114.0	1	88.8
Nitrite	2	85.5	2	83.0	2	96.1
Bromide	1	98.5	1	96.8	1	99.5
Nitrate	2	99.7	0	–	2	101.2
Phosphate	5	104.1	5	96.1	5	104.2
Sulfate	0	–	7	110.7	0	–
Analyte	**Mineral Water 2**		**Lake Water Karlsfelder See**		**River Water Würm**	
	Amount added (mg/L)	Recovery (%)	Amount added (mg/L)	Recovery (%)	Amount added (mg/L)	Recovery (%)
Fluoride	0.2	101.6	0.2	98.5	0.2	98.8
Chloride	1	90.6	0	–	0	–
Nitrite	2	94.5	2	91.2	2	87.2
Bromide	1	97.1	1	98.8	1	97.2
Nitrate	3	101.4	4	101.0	2	96.1
Phosphate	5	103.3	5	100.2	5	103.6
Sulfate	5	105.3	6	108.5	6	108.9

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

Analyte	Drinking Water Karlsfeld		Drinking Water Pitzling		Mineral Water 1	
	Amount added (mg/L)	Recovery (%)	Amount added (mg/L)	Recovery (%)	Amount added (mg/L)	Recovery (%)
Lithium	0.1	89.8	0.1	96.0	0.1	96.9
Sodium	0	–	7	96.6	1	95.5
Ammonium	2	141.8	2	109.0	2	97.6
Potassium	0.5	91.0	2	98.9	0.5	114.2
Magnesium	4	92.9	32	101.9	1	99.2
Calcium	5	86.4	0	–	27	94.9
Analyte	**Mineral Water 2**		**Lake Water Karlsfelder See**		**River Water Würm**	
	Amount added (mg/L)	Recovery (%)	Amount added (mg/L)	Recovery (%)	Amount added (mg/L)	Recovery (%)
Lithium	0.1	96.5	0.1	91.1	0.1	96.1
Sodium	1	100.4	27	96.5	13	97.3
Ammonium	2	95.1	2	142.0	2	–
Potassium	2	115.1	4	96.1	3	106.8
Magnesium	3	102.0	21	101.0	16	100.5
Calcium	6	99.7	0	–	43	95.6

Column: Sykam A09 (75 x 2.6 mm) and Sykam AGC-05 (20 x 2.6 mm)
Eluent: 3.5 mM Na_2CO_3, 25 µM NaSCN
Flow Rate: 1.2 mL/min
Inj. Vol.: 50 µL
Detection: Suppressed Conductivity, Electrochemical Self-Regenerating Anion Suppressor (40 mA)

Peaks:		
1. Fluoride	0.04	0.24 mg/L
2. Chloride	0.95	1.8
3. Nitrite	n.d.	1.9
4. Bromide	0.007 (<MRL)	0.98
5. Nitrate	2.5	5.5
6. Phosphate	0.08	5.2
7. Sulfate	4.1	9.3

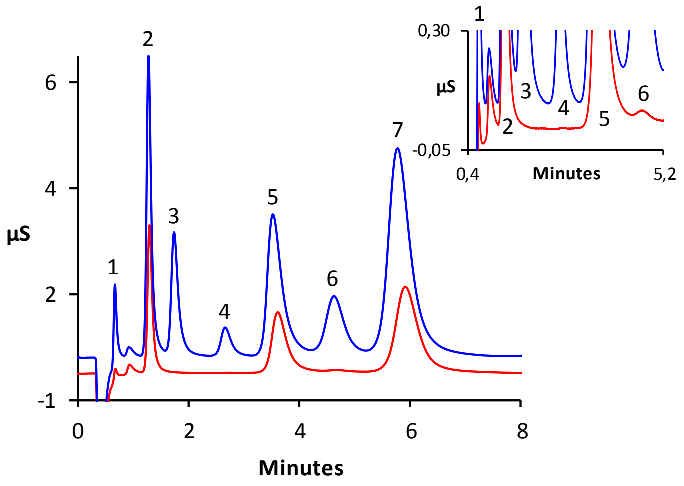

Figure 8. Determination of anions in spiked (blue) and unspiked (red) mineral water 2 samples (undiluted).

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.[8] As the fortification levels for the LFB are above 10x MRL, the specification of ±15% was applied. For the cations the LFB shows excellent recovery rates from 92.0 to 99.9% for most cations. With a recovery of 111.9%, ammonium has the largest deviation of the cations. This is likely because ammonium elutes very close to sodium and its actual peak area is overestimated the more sodium the sample contains. Similarly to ammonium for the cations, nitrite has the largest deviation in the LFB for the anions, with a recovery of 88.3%. The other anions all have excellent recoveries between 96.0 and 106.2 Overall, all recovery values of the LFBs are well within the specification of ±15%.

In the case of the cation recoveries for the LFMs, the values are between 86.4 and 115.1% with most cations deviating no more than ±10%. Only ammonium shows recoveries significantly higher, with 123.2% for the river sample, and even exceeds the specification of ±25% for drinking water 1 and the lake water sample with values of 141.8 and 142.0%. Both of these samples have a high sodium content of about 50 mg/L, showing once again, that ammonium is overestimated at high sodium concentrations. Due to this observation we recommend the use of a longer analytical method, such as the one described in Sykam AN09, for the analysis of small amounts of ammonium next to large concentrations of sodium.

Column: Sykam C08 (250 x 2.6 mm) and Sykam CGC-04 (20 x 2.6 mm)
Eluent: 7.5 mM Methanesulfonic acid
Flow Rate: 1.0 mL/min
Inj. Vol.: 10 µL
Detection: Suppressed Conductivity, Electrochemical Self-Regenerating Cation Suppressor (35 mA)

Peaks:	1. Lithium	0.001 (<MRL)	0.1 mg/L
	2. Sodium	0.8	1.8
	3. Ammonium	n.d.	1.9
	4. Potassium	1.5	3.8
	5. Magnesium	2.4	5.4
	6. Calcium	5.9	11.8

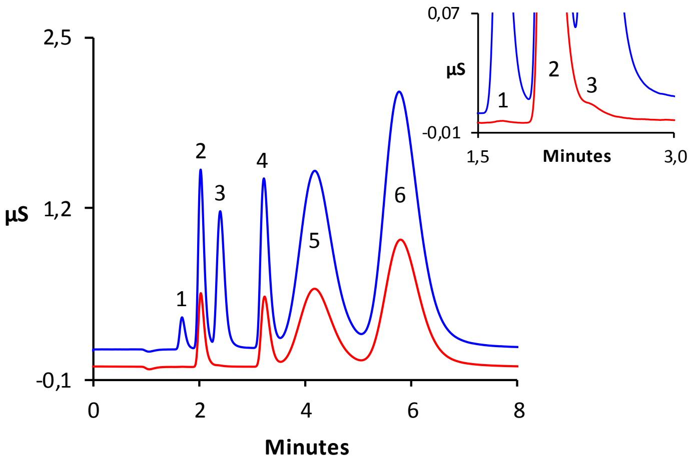

Figure 9. Determination of cations in spiked (blue) and unspiked (red) mineral water 2 samples (undiluted).

For the anions, the recovery rates are all well within the specification of ±25%, with values ranging from 88.8 to 114%. The largest deviations were observed for chloride and nitrite. Similarly to sodium and ammonium, this is likely due to the close retention times of these two anions. While the recoveries were still well within ±25% deviation, better results may be achieved by using an additional UV/Vis detector for the analysis of nitrite, especially when low concentrations are to be analyzed alongside large amounts of chloride. It should be noted, that values of ions which are found below the MRL in the unfortified samples, and are therefore not reported, were still taken into consideration for the calculation of the recovery rate, to increase accuracy.

Summary

The Sykam A09 and C08 columns are suitable for the rapid, simultaneous determination of the standard inorganic anions and cations in natural and drinking waters, using a method with a runtime of only 9 minutes. This method complies with U.S. EPA Method 300.1, ASTM D4327 and EN ISO 10304-1 for anions and ASTM D6919 and EN ISO 14911 for cations, as was shown by a full validation in regards to all specifications given in the mentioned guidelines concerning the determination of method detection limits, resolution, linearity and precision. Good to very good recovery data for the fortified sample matrices as well as for the fortified blank were found under the described chromatographic conditions, especially for anions. For cation analysis, the Sykam C08 column 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 sodium, potassium, magnesium or calcium without the need for sample dilution. Despite the short runtime, the Sykam A09 and C08 columns show high resolution of all examined standard ions, especially for the anions. This makes them suitable for the analyses of complex matrices or samples with large concentration differences between closely eluting peak pairs. The only exception, is in cases where small amounts of ammonium need to be analyzed alongside high levels of sodium. In this case we recommend the use of a longer method, such as the one described in Sykam AN09, using the Sykam C06 column. Additionally, the detection of nitrite alongside large concentrations of chloride may be improved by the use of a UV/Vis detector.

References

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

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[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] 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.

[8] 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.

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

[10] 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.

[11] 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

[12] 40 CFR Appendix -B-to-Part-136 – Definition and Procedure for the Determination of the Method Detection Limit – Revision 2.

[13] 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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