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

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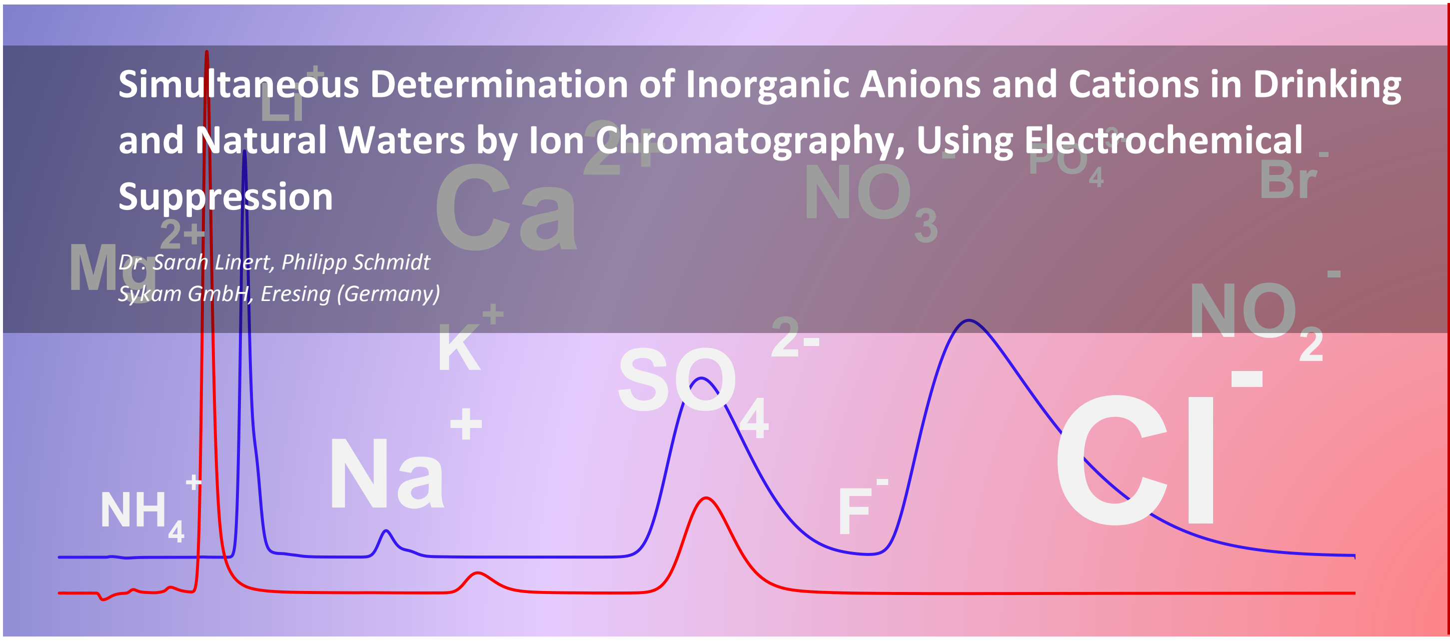

Introduction

With an ever-growing population and corresponding increase in industry, pollution from human sources poses a constant threat to the environment. This not only has adverse effects on the world's ecosystem, but human wellbeing is also at risk. Therefore, in order to protect the environment and the health of the population, many regulations have been put in place around the world to monitor and limit the negative impact human pollution has on the planet. Especially important amongst these regulations are those that protect the quality of drinking water, such as the Drinking Water Directive (DWD) 98/83/EC[1] put in place by the European Union (1998, latest version 2020/2184 from December 2020)[2] and the Safe Drinking Water Act (SDWA)[3] established in the United States. Both these regulations aim to ensure the quality and safety of drinking water for human consumption. The protection of natural waters on the other hand is regulated in the European union by the Water Framework Directive (2000/60/EC)[4] from October 2000, which aims to preserve inland surface waters, transitional waters, coastal waters and groundwaters in order to maintain and enhance the status of aquatic ecosystems. In the United States, the Clean Water Act (CWA) aims to reduce the amount of pollutants that are released into the environment.[5] These amounts are regulated by Maximum Contaminant Levels (MCLs), which are defined in the EU DWD[2] and the U.S. National Primary and Secondary Drinking Water Standards (NPDWS/NSDWS).[6] Similar 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.

In the USA, fluoride, nitrite and nitrate contents are regulated by the National Primary Drinking Water Standards, while chloride and sulfate are categorized as secondary contaminants and are covered by the National Secondary Drinking Water Standards.[6] Similarly, In the EU, these inorganic anions are regulated by the Drinking Water Directive.[2] While the common cations present in drinking and natural waters are not considered primary contaminants in the U.S., they are regulated in the EU and monitored and reported by most suppliers. Also, calcium and magnesium are measured to determine the hardness of water. Among the inorganic cations, ammonium is of special interest as it can dissociate to ammonia in water depending on temperature and pH, becoming toxic to aquatic life at certain degrees of dissociation.[7]

The most commonly used analytical technique for monitoring the quantity of ionic species in drinking and natural water is ion chromatography (IC). 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 AN09" describes the simultaneous determination of inorganic anions and cations in drinking and natural waters 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[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 C06 (100 x 4.6 mm) were used for the method validation and the validation results are discussed within this application note.

Equipment

Application note “Sykam AN09” 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 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 (Milbertshofen, Munich)
2	Drinking Water (Hamlar)
3	Mineral Water 1
4	Mineral Water 2
5	River Water (Isar)
6	Stream Water (Egelseebach)

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 two drinking water samples were collected as tap water from two different municipal water suppliers in Munich and Hamlar. The two mineral water samples were commercially available mineral waters from companies, that obtain their water from natural groundwater sources. The stream water was collected from a stream near Asbach-Bäumenheim and the river water was collected from the river Isar 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 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:	25 min
Temperature:	35 °C
Injection Volume:	50 µL (full loop)
Detection:	Suppressed Conductivity, Electrochemical Self-Regenerating Anion Suppressor
Suppressor Current:	40 mA
Backpressure:	69 bar (1001 psi)
Base Conductivity:	19 µS/cm
Noise:	<3 nS/cm

Method Validation Cations

Columns:	Sykam C06 (100 x 4.6 mm), Analytical Column Sykam CGC-06 (20 x 4.0 mm), Guard Column
Eluent:	5.0 mM Methanesulfonic acid
Flow Rate:	1.0 mL/min
Run Time:	25 min
Temperature:	35 °C
Injection Volume:	10 µL (full loop)
Detection:	Suppressed Conductivity, Electrochemical Self-Regenerating Cation Suppressor
Suppressor Current:	20 mA
Backpressure:	33 bar (479 psi)
Base Conductivity:	1.4 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. In case of 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 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 prepared from the respective salts as indicated above, 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 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 50, 20, 10, 5, 2 and 1 µg/L of each cation is prepared from 10 mg/L single standard solutions.

As mentioned in ASTM D6919[11] and EN ISO 14911,[12] 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 approx. 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, 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). Likewise, for the determination of the linear calibration range of the six standard cations, a mixed cation standard was injected 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 lithium). All concentration levels are prepared from the 1000 mg/L standard stock solutions.

Table 3. Concentrations of MDL_S, 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	75	2	20
Chloride	25	10	100
Nitrite	50	2	100
Bromide	100	2	100
Nitrate	75	20	100
Phosphate	350	2	100
Sulfate	200	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	10	5	100
Potassium	10	10	100
Magnesium	10	20	100
Calcium	10	40	100

To assess the performance of the chromatographic system, External Control Samples (ECS) are prepared at the same concentrations as the QCS. In the case of the anions, self-prepared 1000 mg/L stock solutions (salt amounts used 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 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 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 pressurized with inert gas (optional).

Cations (Sykam C06): 5.0 mM methanesulfonic acid – 649.6 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 1.0 mL/min. 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 1.0 mL/min. 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. 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 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),[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. The methods define that optional columns and corresponding, different chromatographic conditions may be used, to improve the separations or lower the costs of measurement. Here, the Sykam A07 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[13]
- Linearity (Linear Calibration Range, LCR)[14]
- 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 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, Electrochemical Self-Regenerating Anion Suppressor (40 mA)
Peaks: 1. Fluoride 4.0 mg/L
2. Chloride 20.0
3. Nitrite 20.0
4. Bromide 20.0
5. Nitrate 20.0
6. Phosphate 20.0
7. Sulfate 20.0

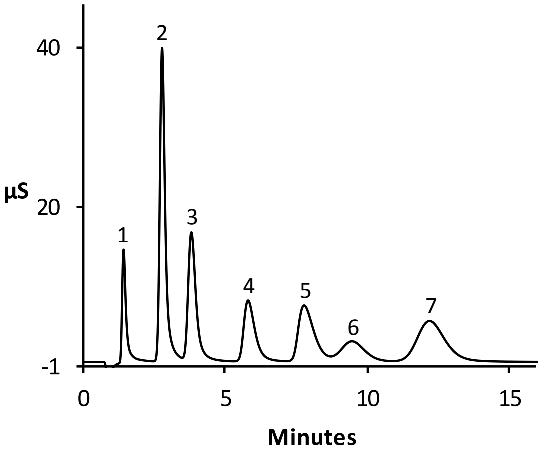

Figure 1. Separation of the 20% calibration standard for inorganic anions.

Table 4. Column performance parameters of Sykam A07 (20% calibration standard) and Sykam C06 (10% calibration standard) at the chromatographic conditions listed above.

Analyte	Retention time (min)	Resolution R	Peak Symmetry
Fluoride	1.43	–	2.07
Chloride	2.78	4.80	1.57
Nitrite	3.81	2.51	1.52
Bromide	5.82	3.33	1.60
Nitrate	7.79	2.30	1.64
Phosphate	9.48	1.32	1.20
Sulfate	12.21	1.64	1.25
Lithium	2.74	–	1.53
Sodium	3.53	2.68	1.62
Ammonium	4.32	2.05	1.43
Potassium	6.18	3.56	1.84
Magnesium	12.68	3.72	1.49
Calcium	18.88	1.91	1.81

Likewise, 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] using the Sykam C06 column under the chromatographic conditions listed above. The same quality control parameters were tested as for the anion method validation.

The Sykam C06 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 standard using the Sykam C06.

Column: Sykam C06 (100 x 4.6 mm) and Sykam CGC-06 (20 x 4.0 mm)
Eluent: 5.0 mM Methanesulfonic acid
Flow Rate: 1.0 mL/min
Inj. Vol.: 10 µL
Detection: Suppressed Conductivity, Electrochemical Self-Regenerating Cation Suppressor (20 mA)
Peaks: 1. Lithium 2.0 mg/L
2. Sodium 10.0
3. Ammonium 10.0
4. Potassium 10.0
5. Magnesium 10.0
6. Calcium 10.0

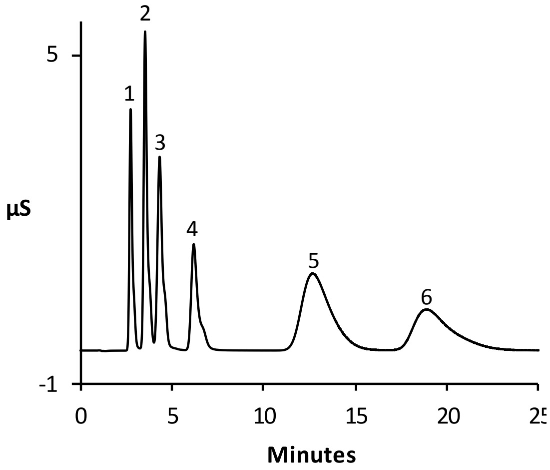

Figure 2. Separation of the 10% calibration standard for inorganic cations.

The peak resolution is R >1.3 for all standard anions and cations (Table 4), as required by EN ISO 10304-1[8] and EN ISO 14911.[12] The columns exhibit good peak symmetry, allowing exact integration of peak areas.

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 of each anion. The same procedure was used to determine the MDL_S of the cations, injecting six mixed cation standards with concentrations of 50, 20, 10, 5, 2 and 1 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 $MDL_S = t \times SD$, 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 chloride was found at a mean level of 2.3 µg/L and sodium at a mean level of 43.7 µg/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: $MDL_B = X + t \times SD$, 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 9.7 µg/L and the MDL_B of sodium to 0.11 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 module 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 ten calibration levels were injected for anions and cations respectively: 0.1, 0.2, 0.5, 1.0, 2.0, 5.0, 10, 20, 50 and 100% of each Standard. 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 which 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 0.02–20 mg/L was determined, which is sufficiently high, as both these ions are only contained in trace amounts (<1.0 mg/L) in natural water samples. Bromide, nitrate, phosphate and sulfate exhibit a linear calibration range of 0.1–50 mg/L, whereas all other measured ions show linear behavior in a range of 0.1–100 mg/L. 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 linear fits exhibit correlation factors of r^2 >0.999 and are considered very accurate. The r^2 value for ammonium is slightly lower than the other values but with 0.998 it is still well within the requirements set by the ASTM D6919.[11]

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	1.0000	4.0	0.36	0.39
Chloride	0.1 – 100	0.9995	5.4*	0.21	0.23
Nitrite	0.1 – 100	1.0000	7.2	0.18	0.90
Bromide	0.1 – 50	0.9996	4.2	0.20	0.58
Nitrate	0.1 – 50	0.9996	15.4	0.15	1.71
Phosphate	0.1 – 50	0.9998	33.4	0.29	1.77
Sulfate	0.1 – 50	0.9997	44.4	0.04	0.47

* 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	0.02– 2	1.0000	5.4	0.21	0.53
Sodium	0.1 – 100	1.0000	3.4*	0.17	0.56
Ammonium	0.1 – 100	0.9981	6.1	0.13	0.45
Potassium	0.1 – 100	1.0000	10.0	0.10	0.50
Magnesium	0.1 – 100	1.0000	5.0	0.09	0.55
Calcium	0.1 – 100	0.9999	3.6	0.09	0.54

* Value not valid, MDL_B is used instead

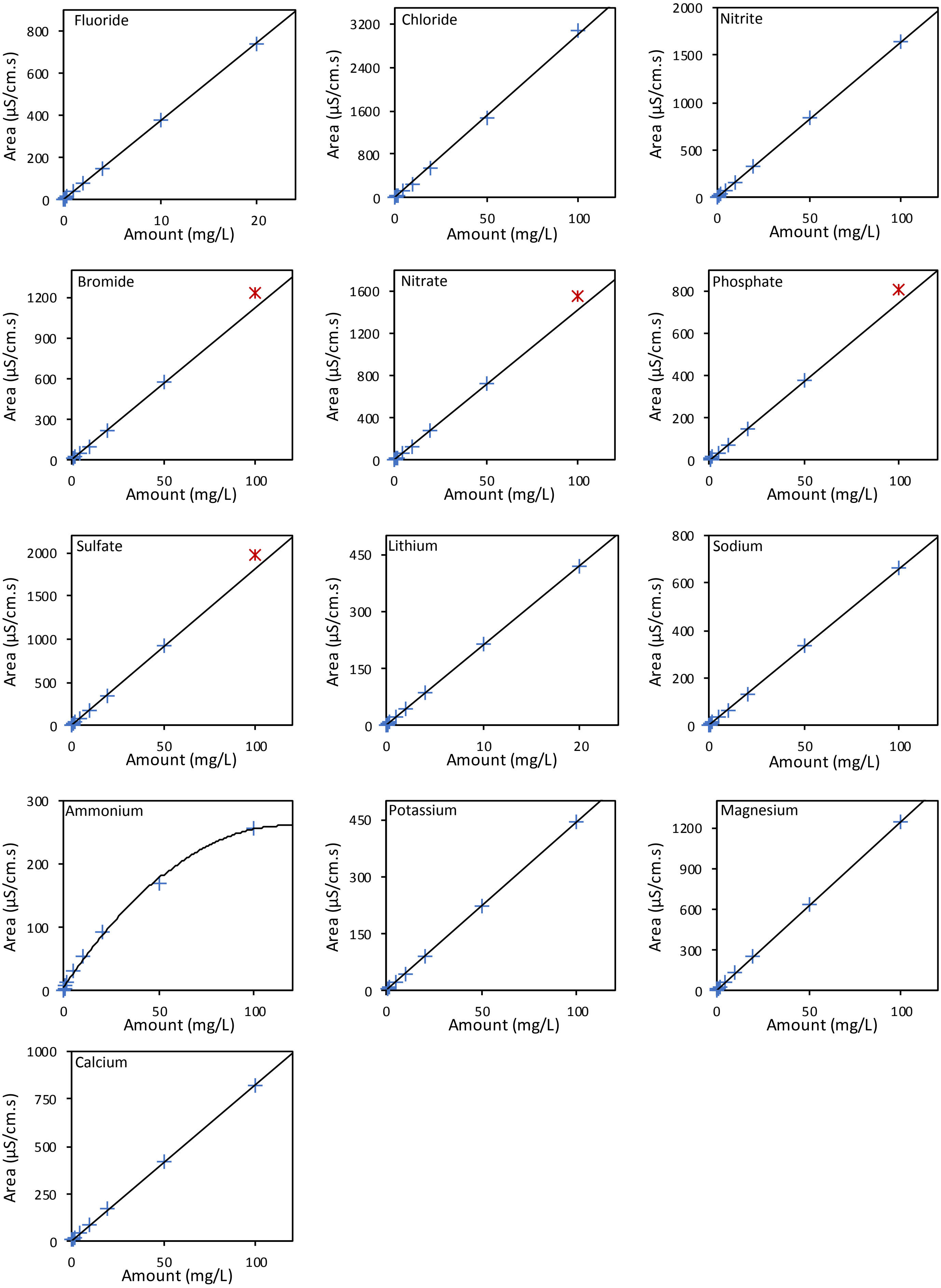

Figure 3. Calibration plots of the standard anions and cations indicating the LCR used for analysis of the samples.

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. For all investigated ions, the RSDs of the retention times are well below 1.0% as are the RSDs of the peak areas, except for nitrate and phosphate, which were found to be considerably lower than the required 2.0%. These values illustrate the high precision achieved with the Sykam S153-AG Dual+ IC system using the Sykam A07 and Sykam C06 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 which were used for the preparation of the calibration standards. If used for verification of the instrument performance, the acceptance range for the ECS in comparison to 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	-1.4
Chloride	-3.5
Nitrite	-6.0
Bromide	-4.2
Nitrate	-6.4
Phosphate	-7.0
Sulfate	-2.8
Lithium	-0.5
Sodium	-1.8
Ammonium	-0.9
Potassium	-2.2
Magnesium	1.9
Calcium	-2.3

Sample Analysis

All six samples (Table 1) were analyzed twice after filtration, as initial sample and duplicate. The concentration of both anions and cations were within the calibration ranges, so all samples were analyzed without dilution. 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. 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 ranges and 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	0.02
Sodium	0.20
Ammonium	0.10
Potassium	0.10
Magnesium	0.10
Calcium	0.10

For the anions, nitrite and phosphate were not detected in any of the six water samples, while bromide was found in very low concentrations below the MRL in half of the samples (2, 4, 6). Low levels of Fluoride were detected in all samples, ranging from 0.08–0.17 mg/L. A wide range of concentrations were measured for chloride from 0.82 mg/L for the first mineral water sample up to 25.0 mg/L in the stream water sample. Similar to chloride, the lowest reported nitrate content was found in mineral water sample 1 at 0.16 mg/L and the highest concentration was detected in drinking water sample 1 at 10.8 mg/L. In mineral water sample 2, nitrate was found at a level below the MRL. The anion with the highest concentrations was found to be sulfate, ranging from 8.3–35.8 mg/L.

For the cations, lithium was detected at values below the MRL in all water samples. Similarly, ammonium was present in half the samples at concentrations below the MRL. Potassium was detected in all samples at low concentrations of 1.0–2.7 mg/L and magnesium at higher levels of 23.8–34.7 mg/L. With 43.6–89.3 mg/L 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 the anions showing a maximum deviance of 2.4 % and calcium and sodium showing a deviance of around 13% for the cations. For mineral water 2 the deviance is in a range of -0.6 to 8.5% for most anions and cations, with the exception of chloride, which shows a large deviance of -22.4%. According to the information provided by the supplier, the results provided on the bottle label are from a measurement from 2019, which may explain differences in ion concentrations, as these may fluctuate over 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, Electrochemical Self-Regenerating Anion Suppressor (40 mA)

Peaks:		
	1. Fluoride	0.08 mg/L
	2. Chloride	11.3
	3. Nitrate	10.8
	4. Sulfate	12.9

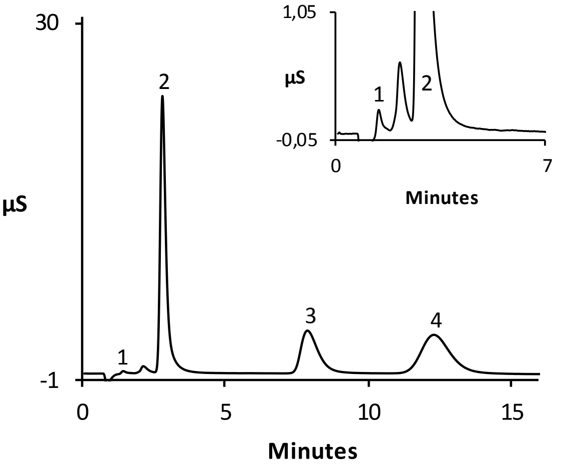

Figure 4. Determination of anions in drinking water (Milbertshofen, Munich).

Column: Sykam C06 (100 x 4.6 mm) and Sykam CGC-06 (20 x 4.0 mm)
Eluent: 5.0 mM Methanesulfonic acid
Flow Rate: 1.0 mL/min
Inj. Vol.: 10 µL
Detection: Suppressed Conductivity, Electrochemical Self-Regenerating Cation Suppressor (20 mA)

Peaks:		
	1. Lithium	0.001 mg/L (<MRL)
	2. Sodium	6.1
	3. Ammonium	0.02 (<MRL)
	4. Potassium	1.4
	5. Magnesium	23.8
	6. Calcium	86.3

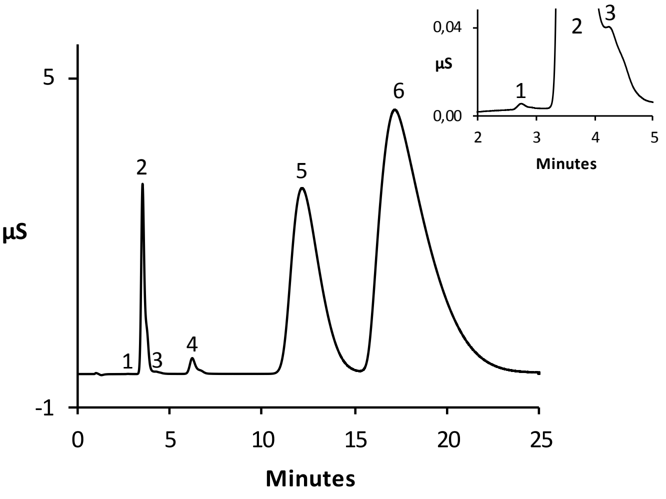

Figure 5. Determination of cations in drinking water (Milbertshofen, Munich).

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, Electrochemical Self-Regenerating Anion Suppressor (40 mA)

Peaks:		
	1. Fluoride	0.17 mg/L
	2. Chloride	16.3
	3. Bromide	0.03 (<MRL)
	4. Nitrate	0.09 (< MRL)
	5. Sulfate	28.8

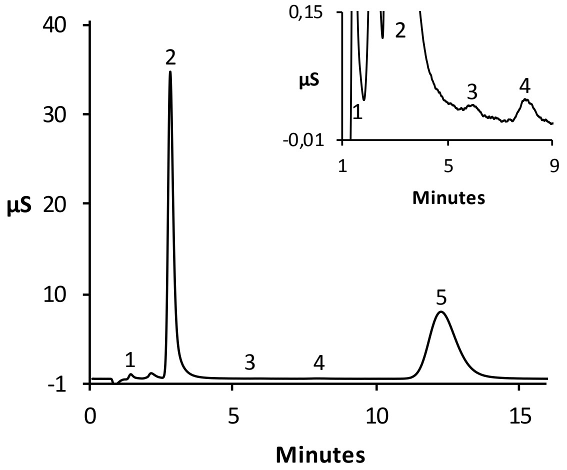

Figure 6. Determination of anions in mineral water 2.

Column: Sykam C06 (100 x 4.6 mm) and Sykam CGC-06 (20 x 4.0 mm)
Eluent: 5.0 mM Methanesulfonic acid
Flow Rate: 1.0 mL/min
Inj. Vol.: 10 µL
Detection: Suppressed Conductivity, Electrochemical Self-Regenerating Cation Suppressor (20 mA)

Peaks:		
	1. Lithium	0.01 mg/L (<MRL)
	2. Sodium	14.0
	3. Potassium	1.2
	4. Magnesium	34.7
	5. Calcium	70.4

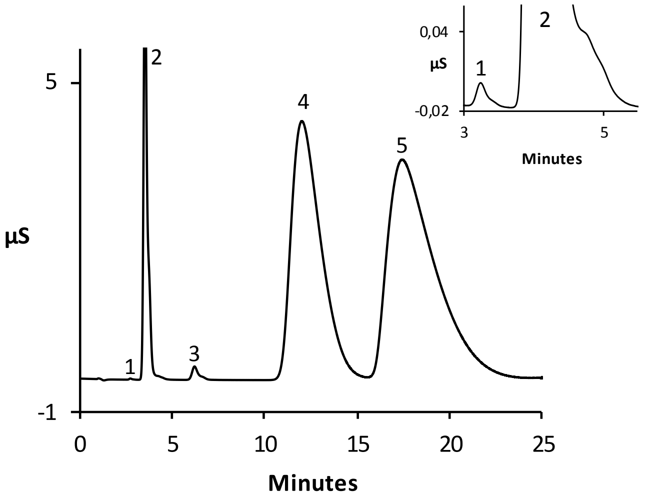

Figure 7. Determination of cations in mineral water 2.

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	0.16	0.16	0.17	0.16
Chloride	0.82	<1.0	16.30	21
Nitrate	0.16	<0.3	<MRL	<0.3
Sulfate	8.30	8.1	28.84	28
Sodium	19.91	17.6	14.02	13.3
Potassium	1.25	1.2	1.15	1.1
Magnesium	24.05	21.2	34.72	32.0
Calcium	43.58	39.7	70.49	70.9

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.[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 Milbertshofen (Munich)	Drinking Water Hamlar	Mineral Water 1
Fluoride	0.08 (4.0)	0.11 (-0.9)	0.16 (-0.6)
Chloride	11.3 (0.0)	17.2 (0.2)	0.82 (2.7)
Nitrite	n.d.	n.d.	n.d.
Bromide	n.d.	<MRL	n.d.
Nitrate	10.8 (-0.2)	9.5 (0.2)	0.16 (11.2)
Phosphate	n.d.	n.d.	n.d.
Sulfate	12.9 (0.3)	31.4 (0.4)	8.3 (0.3)
Analyte	**Mineral Water 2**	**River Water Isar**	**Stream Water Egelseebach**
Fluoride	0.17 (0.6)	0.13 (-4.8)	0.11 (0.9)
Chloride	16.3 (-0.3)	7.9 (-0.9)	25.0 (2.6)
Nitrite	n.d.	n.d.	n.d.
Bromide	<MRL	n.d.	<MRL
Nitrate	<MRL	3.6 (-1.0)	5.7 (2.2)
Phosphate	n.d.	n.d.	n.d.
Sulfate	28.8 (-0.1)	26.8 (-1.2)	35.8 (2.9)

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

Analyte	Drinking Water Milbertshofen (Munich)	Drinking Water Hamlar	Mineral Water 1
Lithium	<MRL	<MRL	<MRL
Sodium	6.1 (0.1)	9.7 (0.1)	19.9 (-0.4)
Ammonium	<MRL	n.d.	n.d.
Potassium	1.3 (7.9)	2.0 (4.0)	1.2 (7.0)
Magnesium	23.8 (-0.2)	25.0 (0.3)	24.0 (-0.1)
Calcium	86.4 (-0.3)	88.4 (0.2)	43.6 (0.0)
Analyte	**Mineral Water 2**	**River Water Isar**	**Stream Water Egelseebach**
Lithium	<MRL	<MRL	<MRL
Sodium	14.0 (-0.1)	6.6 (0.2)	14.9 (-0.2)
Ammonium	n.d.	<MRL	<MRL
Potassium	1.2 (4.4)	1.0 (10.4)	2.7 (2.9)
Magnesium	34.7 (-0.1)	27.2 (0.4)	26.6 (-0.9)
Calcium	70.4 (-0.1)	65.6 (0.0)	89.3 (-1.0)

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%.[9] During the validation, the check standards did not differ by more than 10.8% from the corresponding anion calibration standard and 12.0% from the corresponding cation calibration standard respectively. In most cases, the difference was less than 5% for anions and 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 through 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.[9] The method specifies that the samples should be fortified, ideally at the same concentrations which 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.

Additionally, a Laboratory Blank is fortified at the highest concentration of each ion found in the samples analyzed during the validation (Laboratory Fortified Blank, LFB). 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	98.0
Chloride	30	84.1
Nitrite	2	114.2
Bromide	2	98.6
Nitrate	15	92.3
Phosphate	5	99.3
Sulfate	40	93.8
Lithium	0.1	97.0
Sodium	20	103.9
Ammonium	0.5	105.6
Potassium	3	101.9
Magnesium	35	101.4
Calcium	45	101.3

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

Analyte	Drinking Water Milbertshofen (Munich)		Drinking Water Hamlar		Mineral Water 1	
	Amount added (mg/L)	Recovery (%)	Amount added (mg/L)	Recovery (%)	Amount added (mg/L)	Recovery (%)
Fluoride	0.5	79.7	0.5	78.2	0.5	79.4
Chloride	15	97.7	20	99.7	1	75.2
Nitrite	2	120.9	2	124.5	2	87.5
Bromide	2	88.0	2	87.0	2	89.3
Nitrate	15	102.3	10	96.6	2	94.5
Phosphate	5	96.0	5	93.3	5	87.4
Sulfate	25	102.8	35	110.2*	10	96.8
Analyte	**Mineral Water 2**		**River Water Isar**		**Stream Water Egelseebach**	
	Amount added (mg/L)	**Recovery (%)**	**Amount added (mg/L)**	**Recovery (%)**	**Amount added (mg/L)**	**Recovery (%)**
Fluoride	0.5	78.9	0.5	79.1	0.5	78.0
Chloride	20	98.7	10	91.5	30	99.8
Nitrite	2	124.4	2	117.4	2	124.6
Bromide	2	87.2	2	87.1	2	85.6
Nitrate	2	90.8	4	87.7	6	94.8
Phosphate	5	84.7	5	89.3	5	91.3
Sulfate	30	108.7*	30	108.9*	40	112.0*

* 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 Milbertshofen (Munich)		Drinking Water Hamlar		Mineral Water 1	
	Amount added (mg/L)	Recovery (%)	Amount added (mg/L)	Recovery (%)	Amount added (mg/L)	Recovery (%)
Lithium	0.1	96.0	0.1	95.0	0.1	93.2
Sodium	6	105.6	10	98.7	20	100.0
Ammonium	0.5	110.8	0.5	98.4	0.5	96.8
Potassium	2	107.1	2	94.7	2	106.7
Magnesium	25	104.1	25	97.2	25	97.3
Calcium	–	–	–	–	45	98.6

Analyte	Mineral Water 2		River Water Isar		Stream Water Egelseebach	
	Amount added (mg/L)	Recovery (%)	Amount added (mg/L)	Recovery (%)	Amount added (mg/L)	Recovery (%)
Lithium	0.1	95.5	0.1	94.0	0.1	95.1
Sodium	15	102.6	7	99.9	15	102.1
Ammonium	0.5	94.9	0.5	99.4	0.5	98.0
Potassium	2	111.2	2	100.5	3	109.1
Magnesium	35	100.7	20	99.0	30	101.2
Calcium	–	–	–	–	–	–

The specification for the recoveries given in EPA Method 300.1 is ±25% for the LFM and ±15% for the LFB, if the fortification level of the LFB is >10x MRL.[9] As the fortification levels for the LFBs are above 10x MRL, the specification of ±15% was applied. For the cations the LFB show excellent recovery rates of 97.0 to 105.6% while most anions are within a range of 92.3 to 99.3%. For chloride and nitrite, the recovery rates have a larger deviation, with nitrate's recovery rate at 114.2% and chloride at 84.1%. The recovery rate of chloride is slightly outside of the specification, by 0.9%. The cause of this is likely the fact that the nitrite and chloride peaks are very close to one another. High chloride values alongside small nitrite values therefore lead to merging of the two peaks causing an overestimation of the nitrite concentration and an underestimation of the chloride concentration. Though the chloride value is only barely outside of the specification, it may be advised to use UV detection in addition to conductivity detection, in cases where small levels of nitrite must be quantified alongside high levels of chloride, or to switch to the Sykam A05 or A02 columns, which exhibit better resolution between chloride and nitrite.

In the case of the cation recoveries for the LFMs, the values are once again very good, with recoveries of 93.2 to 111.2%. For the anions, the recovery rates are all well within the specification of ±25%. Once again, an overestimation of the nitrite values is observed with increasing chloride concentrations. For sulfate, four of six samples have a concentration above the calibration range in the fortified samples. Therefore, though these values are reported, they should not be evaluated. It should also 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.

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, Electrochemical Self-Regenerating Anion Suppressor (40 mA)

Peaks:		
1. Fluoride	0.13	0.52 mg/L
2. Chloride	8.0	16.7
3. Nitrite	3.6	2.3
4. Bromide	-	1.7
5. Nitrate	3.6	6.9
6. Phosphate	-	4.5
7. Sulfate	27.0	(58.1)

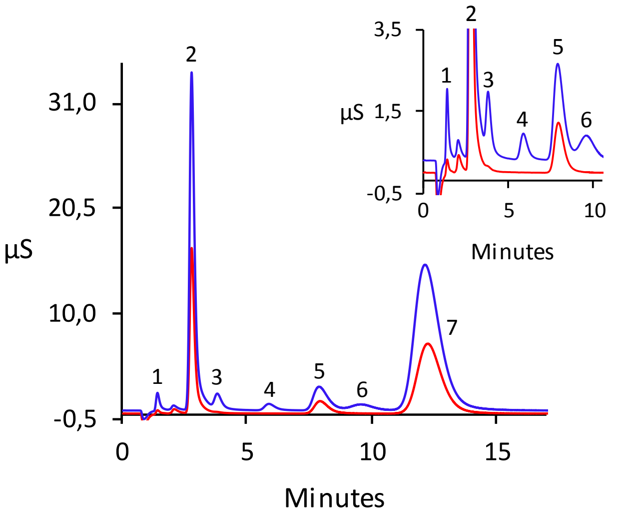

Figure 8. Determination of anions in spiked (blue) and unspiked (red) river water samples (Isar).

Column:	Sykam C06 (100 x 4.6 mm) and Sykam CGC-06 (20 x 4.0 mm)		
Eluent:	5.0 mM Methaensulfonic acid		
Flow Rate:	1.0 mL/min		
Inj. Vol.:	10 µL		
Detection:	Suppressed Conductivity, Electrochemical Self-Regenerating Cation Suppressor (20 mA)		
Peaks:	1. Lithium	0.001 (<MRL)	0.10 mg/L
	2. Sodium	6.7	13.4
	3. Ammonium	0.001 (<MRL)	0.50
	4. Potassium	1.0	3.0
	5. Magnesium	17.1	36.4
	6. Calcium	65.6	62.9

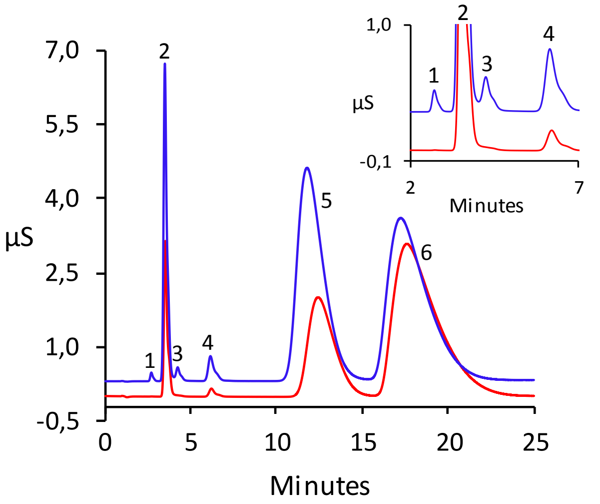

Figure 9. Determination of cations in spiked (blue) and unspiked (red) river water samples (Isar).

Summary

The Sykam A07 and C06 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 EN ISO 10304-1 for anions and ASTM D6919 and EN ISO 14911 for cations. This was shown by a full method validation in regards 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, especially for cations. Both columns exhibit a high capacity, as the linear range was determined over more than two orders of magnitude, making it possible to analyze samples of up to 100 mg/L of chloride and sodium or other inorganic anions without the need for sample dilution. The Sykam A07 as well as the Sykam C06 columns both show high resolution for all examined standard ions, making them suitable for the analyses of complex matrices or large concentration differences between closely eluting peak pairs. For cases where small amounts of nitrite need to be analyzed alongside high levels of chloride, however, the use of an additional UV detector, or the use of the Sykam A05 or A02 columns may be advised.

References

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[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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