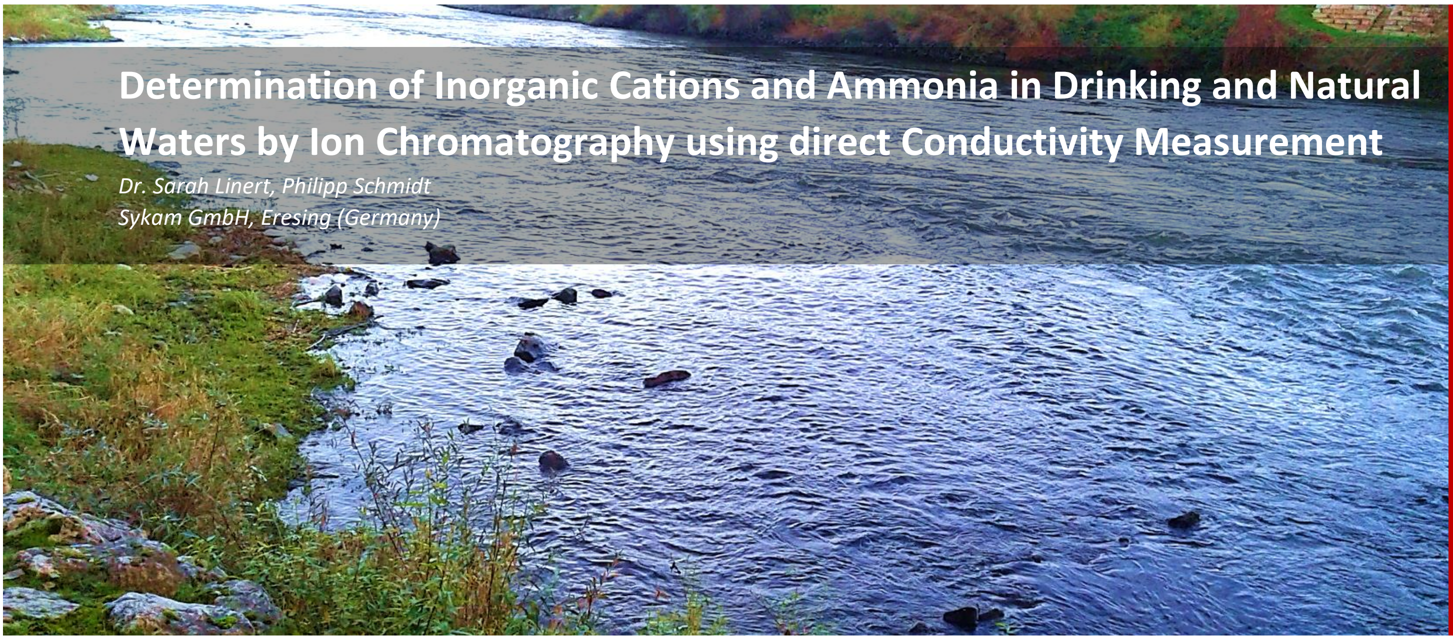

Determination of Inorganic Cations and Ammonia in Drinking and Natural Waters by Ion Chromatography using direct Conductivity Measurement

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Introduction

All over the world the quality of drinking water is monitored to ensure that human health is not affected by pollution from industrial and other human sources. In the European Union, the Drinking Water Directive (DWD) 98/83/EC[1] from 1998 with its latest version 2020/2184[2] published in December 2020 is the respective guideline to ensure water quality. In the United States, water quality is legislated through the Safe Drinking Water Act (SDWA),[3] which ensures the integrity and safety of drinking waters. The European Union established the Water Framework Directive 2000/60/EC[4] in October 2000, which forms the framework for the protection of inland surface waters, transitional waters, coastal waters and groundwater to prevent further deterioration and protect and enhance the status of aquatic ecosystems. The respective primary federal law in the United States is the Clean Water Act (CWA).[5] The content of specific chemicals is regulated by Maximum Contaminant Levels (MCL) e.g. under the EU Drinking Water Directive (DWD)[2] or the U.S. National Primary and Secondary Drinking Water Standards (NPDWS/NSDWS).[6] In most parts of the world, similar health and environmental standards have been established, often by adopting the aforementioned regulations.

In the U.S. the common cations present in drinking and natural waters are not considered primary contaminants, but they are monitored and reported by most suppliers and regulated in the EU. Calcium and magnesium are determined to measure the hardness of water. Ammonium is of special interest since it dissociates to ammonia in water, depending on temperature and pH value. The degree of dissociation determines its toxicity to aquatic life.[7]

Ion chromatography (IC) is one of the most commonly used analytical techniques for the quantification of ionic species in drinking and natural waters. If used for cation analysis, IC allows the determination of alkaline and alkaline earth metals in a single run together with ammonium. National and international standard organizations like the ISO (International Organization for Standardization) and ASTM (American Society for Testing and Materials) have published standards, which are applied for determination of cations in natural and drinking waters. The methods for analysis of cations and ammonium using IC are described in ASTM D6919[8] and EN ISO 14911.[9]

This application note “Sykam AN05” describes the determination of inorganic cations and ammonium in drinking and natural waters by IC using direct conductivity measurement. The method was validated under consideration of the requirements described in the aforementioned methods for cation analysis and therefore provides an economical way to meet the testing requirements of ASTM D6919[8] and EN ISO 14911[9] using a Sykam S152 IC module. The columns Sykam C05 (250 x 8.0 mm) and Sykam C07 (200 x 4.0 mm) were used for the method validation and the validation results are discussed.

The method for cation determination using the Sykam C05 described within this application note AN05 can also be used in place of the Sykam C07 for simultaneous determination of anions and cations as described in application note AN03.

Equipment

Application note Sykam AN05 is designed for use of a Sykam S152-AG IC module with single-channel cation detection consisting of the following components:

- S150 Ion Chromatography Module including column oven and single-channel conductivity detector
- S1130 Quaternary Gradient Pump (PEEK) including 4-channel degasser
- S5300 Automatic Sample Injector with S6115 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.

Instead of the S152-AG IC module a S153-AG Dual IC module can be used in single-channel mode for cation detection. Injections can also be performed using a S6120 Manual Injection Valve in place of the S5300 Automatic Sample Injector. The use of a S1130 isocratic pump instead of a 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
- Methanesulfonic acid (CH_4O_3S, ≥99.0%), Sigma-Aldrich (471356)
- Oxalic acid dihydrate ($C_2H_2O_4 \cdot 2\,H_2O$, ReagentPlus®, ≥99.0%), Sigma-Aldrich (O0376)
- 18-Crown-6 ether (C12H24O6, ≥99.0%), Sigma-Aldrich (80833)
- 2,6-Pyridinedicarboxylic acid ($C_7H_5NO_4$, 99%), Sigma-Aldrich (P63808)
- Lithium standard solution (traceable to SRM from NIST, $LiNO_3$ in 0.5 mol/L HNO_3, 1000 mg/L Li, Certipur®), Merck (1.70223)
- Sodium standard solution (traceable to SRM from NIST, $NaNO_3$ in H_2O, 1000 mg/L Na, Certipur®), Merck (1.19507)
- Ammonium standard solution (traceable to SRM from NIST, NH_4Cl in H_2O, 1000 mg/L NH_4, Certipur®), Merck (1.19812)
- Potassium standard solution (traceable to SRM from NIST, KNO_3 in 0.5 mol/L HNO_3, 1000 mg/L K, Certipur®), Merck (1.70230)
- Calcium standard solution (traceable to SRM from NIST, $Ca(NO_3)_2$ in 0.5 mol/L HNO_3, 1000 mg/L Ca, Certipur®), Merck (1.19778)
- Magnesium standard solution (traceable to SRM from NIST, $Mg(NO_3)_2$ in 0.5 mol/L HNO_3, 1000 mg/L Mg, Certipur®), Merck (1.19788)

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

- Lithium nitrate ($LiNO_3$, anhydrous, extra pure, SLR), Fisher Chemical (10568620)
- Sodium nitrate ($NaNO_3$, for analysis EMSURE, ACS, ISO, Reag. Ph Eur), Merck (1.06537)
- Ammonium chloride (NH_4Cl, Suprapur®), Merck (1.01143)
- Potassium nitrate (KNO_3, ACS reagent, ≥99.0%), Sigma-Aldrich (221295)
- Calcium nitrate tetrahydrate ($Ca(NO_3)_2 \cdot 4\,H_2O$, for analysis EMSURE, ACS, ISO, Reag. Ph Eur), Merck (1.02121)
- Magnesium nitrate hexahydrate ($Mg(NO_3)_2 \cdot 6\,H_2O$, ACS reagent, 99%), Sigma-Aldrich (237175)

Samples

For the method validation, six water samples were analyzed.

Table 1. List of analyzed samples.

No.	Name
1	Drinking Water (Straubing)
2	Drinking Water (Hamlar)
3	Mineral Water 1
4	Mineral Water 2
5	Stream Water (Windach)
6	Lake Water (Eresing)

All six water samples were collected in Southern Germany in the northern foothills of the Alps. Four of the samples were drinking water samples, whereas the remaining two samples are natural surface water samples. The two drinking water samples were collected as tap water from two different municipal water suppliers in Straubing and Hamlar. The two mineral water samples were commercially available mineral waters from companies, which obtain the water from natural ground water sources. The stream water was collected from the Windach near Windach and the lake water was collected from a ground water fed pond near Eresing. All samples were collected in 1000 mL PE-bottles with screw cap and stored at 4 °C immediately after collection.

Chromatographic Conditions

Method Validation 1 (Sykam C05)

Columns:	Sykam C05 (250 x 8.0 mm), Analytical column Sykam CGC-05 (20 x 8.0 mm), Guard column
Eluent:	2.0 mM Methanesulfonic acid, 1.5 mM Oxalic acid, 60 mg/L 18-Crown-6 ether
Flow Rate:	1.5 mL/min
Run Time:	27 min
Temperature:	35 °C
Injection Volume:	10 µL (full loop)
Detection:	Non-suppressed Conductivity (Inverted Signal)
Backpressure:	64 bar (930 psi)
Base Conductivity:	990 µS/cm
Noise:	<30 nS/cm

Method Validation 2 (Sykam C07)

Columns:	Sykam C07 (200 x 4.0 mm), Analytical column Sykam CGC-07 (50 x 4.0 mm), Guard column
Eluent:	2.0 mM Oxalic acid, 3.5 µM 2,6-Pyridine-dicarboxylic acid
Flow Rate:	1.0 mL/min
Run Time:	22 min
Temperature:	35 °C
Injection Volume:	10 µL (full loop)
Detection:	Non-suppressed Conductivity (Inverted Signal)
Backpressure:	83 bar (1200 psi)
Base Conductivity:	1180 µS/cm
Noise:	<50 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. Since cation detection is non-suppressed, the cation signal needs to be inverted by clicking the box “Reverse Signal” in the “Acquisition” Tab of the “Method Setup” window to obtain positive peaks for integration.

To achieve reproducible results, only full loop injections were performed.

Preparation of Solutions and Reagents

Standard Stock Solutions (1000 mg/L)

The standard stock solutions of 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. If 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)
Lithium	Lithium nitrate ($LiNO_3$)	9.933
Sodium	Sodium nitrate ($NaNO_3$)	3.697
Ammonium	Ammonium chloride (NH_4Cl)	2.965
Potassium	Potassium nitrate (KNO_3)	2.586
Calcium	Calcium nitrate tetrahydrate ($Ca(NO_3)_2 \cdot 4\ H_2O$)	5.892
Magnesium	Magnesium nitrate hexahydrate ($Mg(NO_3)_2 \cdot 6\ H_2O$)	10.547

Working Standard Solutions

All single and composite working standard solutions at concentrations lower than 1000 mg/L are prepared from the standard stock solutions and should be prepared fresh daily.

As mentioned in EN ISO 14911[9] and ASTM D6919[8] a low pH value of the sample can interfere with analysis. Since most of the commercially available 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. The use of highly acidic stock solutions results in peak splitting of the alkaline earth metals at concentrations of more than 40 mg/L when using the Sykam C05, especially in the presence of high amounts of nitrate. Therefore, standard stock solutions used for method validation of the Sykam C05 were prepared from the corresponding salts as described above, while commercially available standard stock solutions were used for method validation of the Sykam C07.

For the estimation of the method detection limits of the cations a series of mixed standards at concentrations of 2000, 1000, 500, 400, 300, 200, 100, 50, 20 and 10 µg/L of each cation is prepared from 10 mg/L single standard solutions.

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

For the determination of the linear calibration range of the six standard cations covering the expected concentrations of drinking and natural water samples, nine calibration levels of a mixed cation standard were injected. The concentration levels were 0.2, 0.5, 1, 2, 5, 10, 20, 50 and 100% of the maximum cation standard concentration as listed in table 3. All concentration levels are prepared from the 1000 mg/L standard stock solutions.

Table 3. Concentrations of MDL$_S$, QCS and 100% linearity standard.

Analyte	MDL$_S$ Calculation Standard (µg/L) 10 µL Injection Volume		MDL$_S$ Calculation Standard (µg/L) 100 µL Injection Volume		QCS for Precision (mg/L)		Maximum Standard Concentration (mg/L)	
	Sykam C05	Sykam C07	Sykam C05	Sykam C07	Sykam C05	Sykam C07	Sykam C05	Sykam C07
Lithium	100	100	20	20	2	2	20	2
Sodium	500	250	50	150	15	15	100	50
Ammonium	500	1000	150	75	5	5	100	10
Potassium	5000	1500	1500	250	10	10	100	20
Magnesium	750	1500	350	400	20	20	100	30
Calcium	7500	1500	1500	750	40	40	100	50

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

Eluent solutions

The eluents are prepared from eluent stock solutions. For a 1.00 mol/L oxalic acid stock solution dissolve 12.61 g of oxalic acid dihydrate in 80 mL of deionized water in a 100 mL volumetric flask. Mix the solution thoroughly until completely clear and fill up the flask to the mark, when the solution has come to room temperature. For a 50 mg/L 18-crown-6 ether stock solution dissolve 2.50 g of 18-crown-

6 ether in 40 mL of deionized water in a 50 mL volumetric flask and fill it to the mark in the same manner.

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

Sykam C05: 2.0 mM methanesulfonic acid, 1.5 mM oxalic acid, 60 mg/L 18-crown-6 ether – Add 259.6 µL of methanesulfonic acid, 3.0 mL of the oxalic acid stock solution and 2.4 mL of the 18-crown-6 ether stock solution to 2000 mL of deionized water. Mix the solution thoroughly and filter the eluent over a 0.45 µm regenerated cellulose filter disc. Transfer the eluent to the S7150 Reagent Organizer and pressurize the container with inert gas (optional).

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

Preparation of the IC system

If using a new column, install the column and condition it at a flow rate of 0.3 mL/min of the respective eluent before slowly increasing the flow rate to the desired value. To achieve reproducible results, the system has to warm up and be equilibrated. For equilibration, switch on the column oven at the respective temperature. Apply the desired flow rate until the baseline has stabilized. The baseline noise should be <50 nS/cm. If the system has not been in use for several days or longer, let it equilibrate for 3 hours, if the system is used on a daily basis, let the column oven switched on overnight and apply a low flow rate (0.1 mL/min), so that the system can readily be used for the following analyses. 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 operation manuals.

Sample Preparation

All drinking and natural water samples were degassed under vacuum for approx. 10 minutes prior to analysis. In the laboratory the samples were divided into an initial sample and a laboratory duplicate. The duplicate sample was treated identical to the initial sample to control the precision of the laboratory procedures. Samples have to be filtered through an appropriate syringe filter (0.45 µm regenerated cellulose) discarding the first 1.0 mL of the filtrate to make sure that no particles can block the capillaries. 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 cations in drinking and natural waters was performed according to the regulations listed in ASTM D6919[8] and EN ISO 14911,[9] so that all requirements of these methods regarding quality control parameters are met. The methods define that different cation exchange columns and corresponding different chromatographic conditions may be used. Here, the Sykam C05 and Sykam C07 columns together with the Sykam S152-AG IC module under the chromatographic conditions listed above were used for the validation, so that all required quality control parameters were tested. This includes the determination of method detection limits MDL_S and MDL_B,[10] Linearity (Linear Calibration Range, LCR),[11] Precision by repeated injection of a Quality Control Sample (QCS), laboratory performance by injection of a laboratory reagent blank (LRB) and laboratory fortified blank (LFB), analysis of duplicates, and assessing analyte recovery by injection of Laboratory Fortified Matrices (LFM) for each sample. Instrument performance was checked throughout the entire sequence by analysis of initial, continuing and end calibration check standards.

The Sykam C05 is a weak cation exchange column based on polybutadiene/maleic acid coated spherical silica with a particle size of 5 µm. Figure 1 shows the separation of an inorganic cation standard using the Sykam C05.

Column: Sykam C05 (250 x 8.0 mm) and Sykam CGC-05 (20 x 8.0 mm)
Eluent: 2.0 mM Methanesulfonic acid, 1.5 mM Oxalic acid, 60 mg/L 18-Crown-6 ether
Flow Rate: 1.5 mL/min
Inj. Vol.: 10 µL
Detection: Non-suppressed Conductivity

Peaks:		
	1. Lithium	4.0 mg/L
	2. Sodium	20.0
	3. Ammonium	20.0
	4. Potassium	20.0
	5. Magnesium	20.0
	6. Calcium	20.0

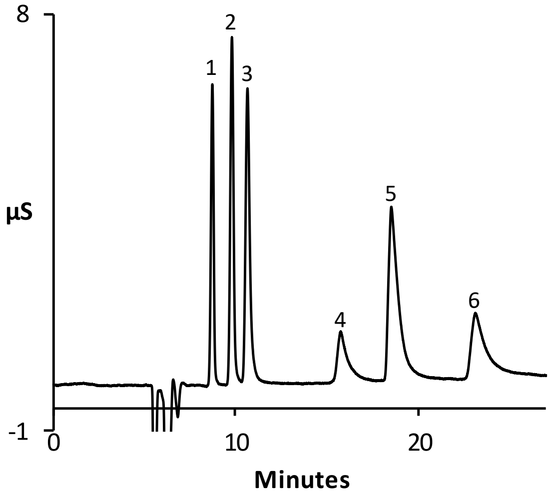

Figure 1. Separation of the 20% calibration standard for inorganic cations using the Sykam C05.

Table 4. Column performance parameters of Sykam C05 (20% calibration standard) and Sykam C07 (20% calibration standard) at the chromatographic conditions listed above.

Analyte	Retention Time (min)		Resolution R		Peak Symmetry	
	Sykam C05	Sykam C07	Sykam C05	Sykam C07	Sykam C05	Sykam C07
Lithium	8.71	3.46	–	–	0.98	1.28
Sodium	9.78	4.35	3.47	4.65	1.10	1.23
Ammonium	10.64	4.83	2.31	2.18	1.40	1.38
Potassium	15.74	6.58	7.80	6.48	2.10	1.26
Magnesium	18.51	17.13	3.03	5.50	2.42	2.08
Calcium	23.09	11.44	4.13	8.34	2.69	2.27

The Sykam C07 is a weak cation exchange column based on a functionalized EVB-DVB resin with a particle size of 7 µm. Figure 2 shows the separation of an inorganic cation standard using the Sykam C07. Due to the presence of 2,6-pyridine-dicarboxylic acid in the eluent, the order of the elution of the alkaline earth metals is reversed in comparison to the Sykam C05. Therefore, in the chromatograms obtained with the Sykam C07 the calcium peak is observed before the magnesium peak.

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

Peaks:	1. Lithium	0.4 mg/L
	2. Sodium	10.0
	3. Ammonium	2.0
	4. Potassium	4.0
	5. Calcium	10.0
	6. Magnesium	6.0

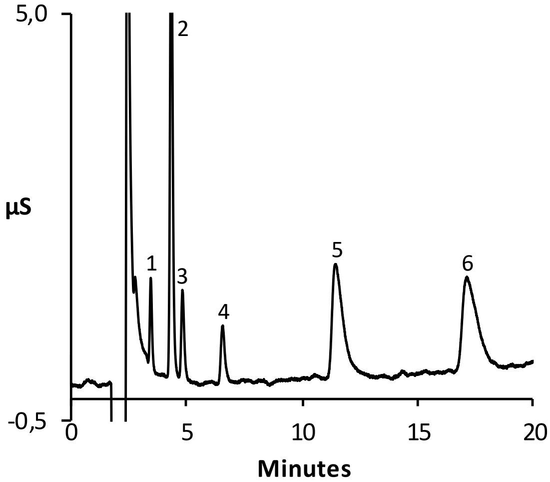

Figure 2. Separation of the 20% calibration standard for inorganic cations using the Sykam C07.

The peak resolution is R >1.3 for all standard cations (Table 4) on both columns, as required in EN ISO 14911,[9] which allows exact integration of peak areas, since all peaks are baseline-separated.

Method Detection Limits MDL$_S$ and MDL$_B$

First, the method detection limits based on sample injection (MDL$_S$) were estimated. Therefore, seven mixed cation standards with concentrations of 2000, 1000, 500, 200, 100, 50 and 20 µg/L per cation were injected. 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 standard. The MDL$_S$ was then calculated as MDL$_S$ = *t* x *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. [10] The thus obtained method detection limits are listed in tables 5 and 6. 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.[10] In this case, seven replicates of the LRB were analyzed with the result that none of the cations were found in any of the LRB injections.

Both columns exhibit a low capacity and therefore a low injection volume of 10 µL was used for the method validation to allow the determination of higher concentrations of the earth alkaline metals without dilution of the samples. Due to this low injection volume the method detection limits are relatively high, especially in case of the later eluting earth alkaline metals and potassium. If the samples are known to contain only small amounts of the analytes a larger injection volume may be applied to improve the sensitivity of the analysis. During this method validation the estimation and determination of the MDLs was repeated under the same chromatographic conditions as mentioned above, performing 100 µL full loop injections instead of 10 µL injections. For the estimation of the MDLs at 100 µL injection volume seven mixed cation standards with concentrations of 1000, 500, 200, 100, 50, 20 and 10 µg/L per cation were injected. The concentrations of the corresponding MDL$_S$-Calculation standards are listed in table 3 and the thus obtained method detection limits in tables 5 and 6. As expected the calculated MDLs are significantly lower, if a larger injection volume is applied, except for the MDLs of sodium and ammonium using the Sykam C05. This effect is more pronounced for the Sykam C07 than the Sykam C05. Due to the smaller inner diameter of the Sykam C07, better results are obtained for low concentrations at an injection volume of 100 µL than using the Sykam C05.

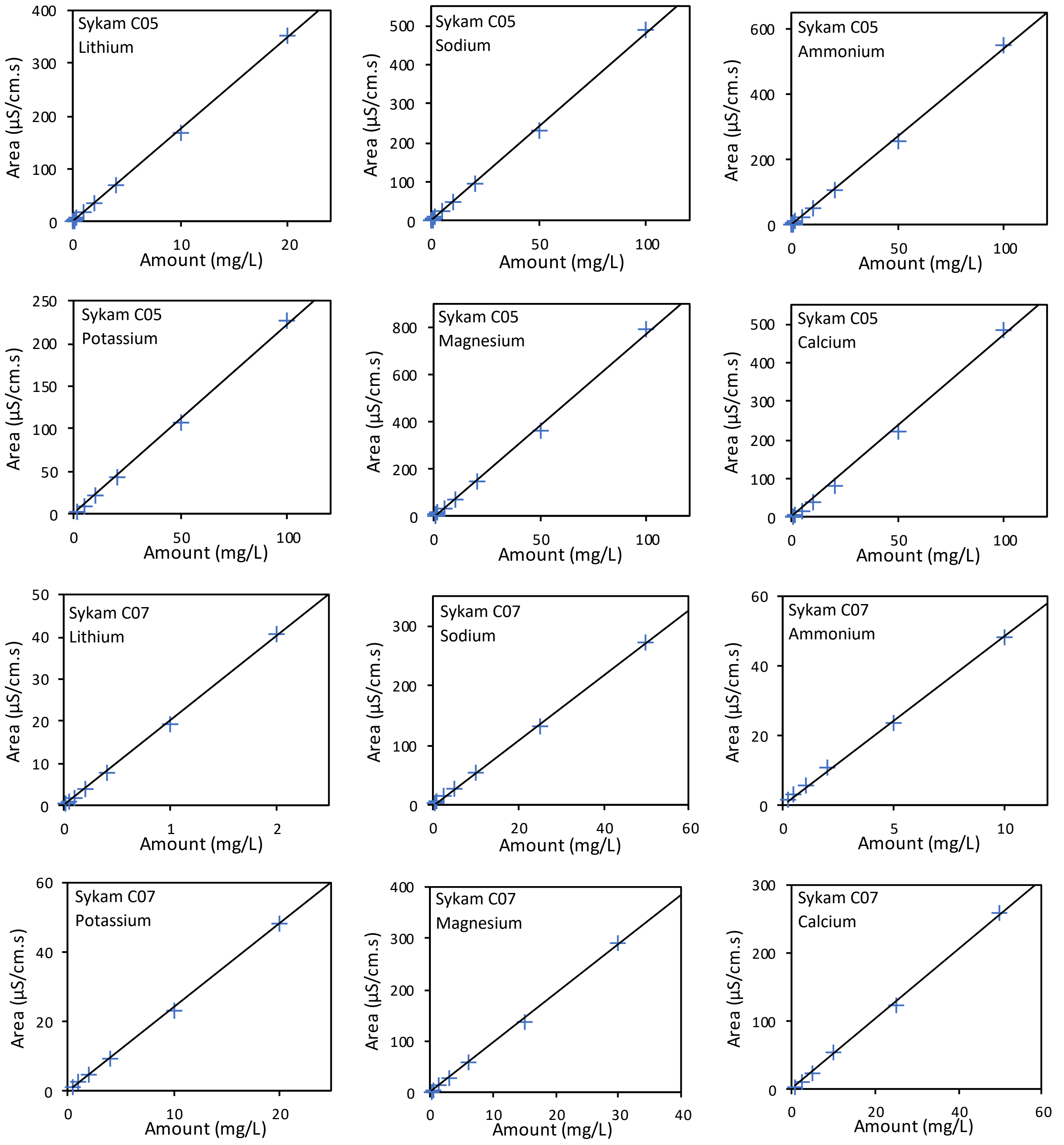

Figure 3. Calibration plots of the standard cations indicating the LCR used for analysis of the samples

Linearity (LCR)

For the assessment of the linear calibration range of cations mixed cation standards at nine calibration levels were injected: 0.2, 0.5, 1, 2, 5, 10, 20, 50 and 100% of the maximum cation standard concentration as listed in table 3. In case of the Sykam C07 the 0.2% standard was omitted, since the concentrations in this standard are mostly below the corresponding MDLs of the respective cations. Figure 3 shows the linear calibration plots for all cations. Calibration points, which are below the calculated $\mathrm{MDL_S}$ are omitted.

In case of the Sykam C05 all cations except for lithium were calibrated up to 100 mg/L. Since lithium is expected to be present only in small amounts in natural and drinking water samples, it was calibrated in a smaller concentration range of 0.04–20 mg/L.

If using the Sykam C07, sodium and calcium exhibit a linear calibration range of 0.25–50 mg/L and 1.0–50 mg/L respectively. Magnesium was calibrated in the concentration range of 0.3–30 mg/L. Higher concentrations of alkaline earth metals than chosen for this calibration exceed the capacity of the Sykam C07 and impair the recovery of the alkaline metals, especially lithium. The calibration of potassium covers the range of 0.4–20 mg/L. The content of lithium and ammonium in drinking and natural water samples is expected to be in the low single digit mg/L or sub-mg/L range and therefore smaller concentration ranges of 0.02–2 mg/L and 0.2–10 mg/L respectively were used for the determination of these cations.

In tables 5 and 6 the linear calibration ranges as well as the correlation factors r^2 of the linear fits for all ions are listed. All linear fits exhibit correlation factors of $r^2 > 0.995$ as required in ASTM D6919[8] and are considered very accurate.

Table 5. Linearity, MDL_S, retention time and peak area precision for the Sykam C05.

Analyte	Calibration Range (mg/L)	Linearity (r^2)	Calculated MDL_S (µg/L) 10 µL Injection Volume	Calculated MDL_S (µg/L) 100 µL Injection Volume	Retention Time Precision (RSD, %)	Peak Area Precision (RSD, %)
Lithium	0.04–20	0.9997	24.9	15.5	0.05	1.04
Sodium	0.2–100	0.9997	29.4	46.0	0.03	1.15
Ammonium	0.2–100	0.9996	57.6	69.9	0.05	2.09
Potassium	2.0–100	0.9997	246.3	67.7	0.10	3.71
Magnesium	0.5–100	0.9991	259.3	106.3	0.04	1.67
Calcium	1.0–100	0.9989	490.4	255.2	0.03	1.99

Table 6. Linearity, MDL_S, retention time and peak area precision for the Sykam C07.

Analyte	Calibration Range (mg/L)	Linearity (r^2)	Calculated MDL_S (µg/L) 10 µL Injection Volume	Calculated MDL_S (µg/L) 100 µL Injection Volume	Retention Time Precision (RSD, %)	Peak Area Precision (RSD, %)
Lithium	0.02–2.0	0.9997	17.2	8.5	0.15	1.95
Sodium	0.25–50	0.9998	81.1	14.8	0.13	1.08
Ammonium	0.20–10	0.9997	148.0	44.8	0.10	1.68
Potassium	0.40–20	0.9998	389.5	79.7	0.12	2.23
Magnesium	0.30–30	0.9997	213.7	55.1	0.10	1.50
Calcium	1.0–50	0.9996	782.1	108.6	0.11	1.44

Precision (QCS) and Instrument Performance (ECS)

Retention time and peak area precision was determined from seven replicate injections of a Quality Control Standard (QCS). Ideally the concentration of the single inorganic ions in the QCS is similar to those found in the field samples and is displayed in Table 3. Tables 5 and 6 show the results of the Relative Standard Deviation (RSD) of retention time and peak area after seven replicate injections of the QCS. The RSD of the retention time is well below 1.0% for both columns and the RSD of the peak areas was found to be less than 4.0% for all investigated ions. The highest values for peak area RSD are obtained for potassium, which is 3.71% for the Sykam C05 and 2.23% for the Sykam C07. All other values are significantly lower.

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, in case of the Sykam C07, the instrument performance was verified by analysis of an External Calibration Standard (ECS). The ECS is prepared from 1000 mg/L single anion standard stock solutions, which are prepared from a different source than the standard stock solutions used for the calibration. The QCS, however is prepared from the same standard stock solutions that were used for the preparation of the calibration standards. 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 a deviation range of ±10%.

Table 7. Relative Percent Differences (RPD) of QCS and ECS for the Sykam C07.

Analyte	RPD (%)
Lithium	-2.9
Sodium	-1.7
Ammonium	8.0
Potassium	7.6
Magnesium	1.9
Calcium	1.4

Sample Analysis

All six samples were analyzed undiluted after filtration, each as laboratory duplicate. Since the amount of calcium found in mineral water 1 was not covered by the calibration range for the Sykam C05, analysis of this sample was repeated after dilution of the sample in a 1:1 ratio with deionized water. The calcium contents of the two drinking water samples and mineral water 1, as well as the stream and lake water were above the highest calibration level of the Sykam C07. Therefore, these samples were diluted with deionized water and the analysis was repeated with the diluted samples to obtain valid results for cation analysis. The drinking water samples as well as the stream and water samples were diluted in a 1:1 ratio, while mineral water 1 was diluted in a 1:2 ratio.

Table 8. Analysis results (mg/L) and RPD (%) of duplicate analyses of both validations.

Analyte	Drinking Water Straubing		Drinking Water Hamlar		Mineral Water 1	
	Sykam C05	Sykam C07	Sykam C05	Sykam C07	Sykam C05	Sykam C07
Lithium	0.044 (0.0)	< MRL	n.d.	n.d.	n.d.	< MRL
Sodium	54.9 (-0.1)	55.6 (1.0)	9.3 (-2.1)	9.6 (0.0)	14.6 (-7.1)	9.0 (2.3)
Ammonium	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Potassium	3.3 (4.5)	3.8 (-14.1)	3.1 (5.6)	2.4 (6.6)	3.6 (-0.7)	2.8 (-10.2)
Magnesium	23.5 (0.0)	22.8 (2.6)	24.6 (-1.9)	24.2 (-6.7)	54.8 (-0.3)	56.4 (0.1)
Calcium	78.1 (-1.4)	67.2 (-0.6)	84.6 (-0.1)	73.6 (-0.5)	122.6 (-0.7)	101.1 (0.7)

Analyte	Mineral Water 2		Stream Water Windach		Lake Water Eresing	
	Sykam C05	Sykam C07	Sykam C05	Sykam C07	Sykam C05	Sykam C07
Lithium	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Sodium	12.5 (0.8)	12.3 (-1.6)	9.8 (2.9)	9.8 (3.9)	37.1 (0.0)	29.4 (-0.4)
Ammonium	n.d.	n.d.	n.d.	n.d.	< MRL	n.d.
Potassium	5.2 (-11.3)	6.4 (1.1)	2.7 (0.9)	1.6 (2.0)	6.4 (6.7)	6.0 (-3.4)
Magnesium	8.0 (-3.7)	8.4 (-3.5)	27.8 (7.0)	26.0 (-0.3)	20.6 (-0.2)	14.4 (-3.4)
Calcium	10.4 (3.4)	10.2 (5.3)	102.8 (0.8)*	86.4 (1.5)	70.7 (2.2)	45.0 (3.8)

* Concentration is above the highest calibration level

Table 8 gives an overview of the analysis results for the six drinking and natural water samples, listing the mean value of the duplicate analysis and their Relative Percent Difference (RPD). The results found for the diluted samples are multiplied by the corresponding dilution factors to obtain the overall cation content of the samples. This is also necessary for comparison of the results obtained with the different columns.

Table 9. Minimum Reporting Levels based on the LCR and MDL.

Analyte	MRL (mg/L) Sykam C05	MRL (mg/L) Sykam C07
Lithium	0.04	0.02
Sodium	0.20	0.25
Ammonium	0.20	0.20
Potassium	2.0	0.40
Magnesium	0.50	0.30
Calcium	1.0	1.0

Lithium and ammonium were not detected in most of the drinking and natural water samples. If detected, these ions were found only in very low concentrations near or below the Minimum Reporting Level (MRL). The MRL is defined as the lowest concentration, at which an analyte can be quantified. The MRL is higher or equal to the lowest calibration concentration and has to be higher than the MDL. Table 9 gives an overview of the MRLs for each cation based on the applied linear calibration range and the calculated MDLs. Potassium was found only in low concentrations between 1.6–6.4 mg/L. The detected concentrations of sodium and magnesium range from 9.0–55.6 mg/L and 8.0–56.4 mg/L respectively. The amounts of calcium in the drinking and natural waters vary over a wide range of 10.2–122.6 mg/L. If high amounts of alkaline earth metals are present in the samples, the values obtained using the Sykam C07 are generally lower than those measured with the Sykam C05.

The values found in the laboratory duplicates do not differ significantly from the respective initial samples, which indicates the robustness of the validated method. The 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.

Table 10 summarizes the found results 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. The analysis results of mineral water 2 reported by the supplier are very similar to those found during this validation on both columns. For mineral water 1 the determined values obtained with the Sykam C05 correspond well with the analysis results given by the supplier as shown in table 10, while the amount of calcium found using the Sykam C07 is too low. This indicates that the values obtained with the Sykam C05 are more reliable for high concentrations of alkaline earth metals.

Table 10. 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		
	Sykam C05	Sykam C07	Supplier	Sykam C05	Sykam C07	Supplier
Sodium	14.6	13.5	16.8	12.5	12.3	12
Potassium	3.6	2.8	3.3	5.2	6.4	6
Magnesium	54.8	50.4	57	8.0	8.4	8
Calcium	122.6	101.1	132	10.4	10.2	12

Column: Sykam C05 (250 x 8.0 mm) and Sykam CGC-05 (20 x 8.0 mm)
Eluent: 2.0 mM Methanesulfonic acid, 1.5 mM Oxalic acid, 60 mg/L 18-Crown-6 ether
Flow Rate: 1.5 mL/min
Inj. Vol.: 10 µL
Detection: Non-suppressed Conductivity
Peaks: 1. Sodium 9.3 mg/L
2. Potassium 3.1
3. Magnesium 24.6
4. Calcium 84.6

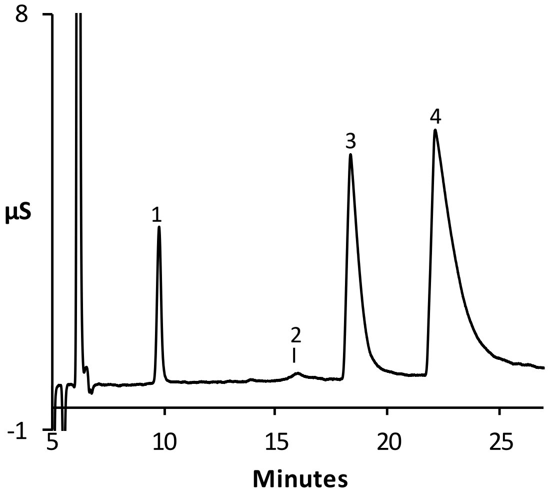

Figure 4. Determination of cations in drinking water (Hamlar) using the Sykam C05.

Column: Sykam C05 (250 x 8.0 mm) and Sykam CGC-05 (20 x 8.0 mm)
Eluent: 2.0 mM Methanesulfonic acid, 1.5 mM Oxalic acid, 60 mg/L 18-Crown-6 ether
Flow Rate: 1.5 mL/min
Inj. Vol.: 10 µL
Detection: Non-suppressed Conductivity
Peaks: 1. Sodium 7.3 mg/L
2. Potassium 1.8
3. Magnesium 27.4
4. Calcium 61.3

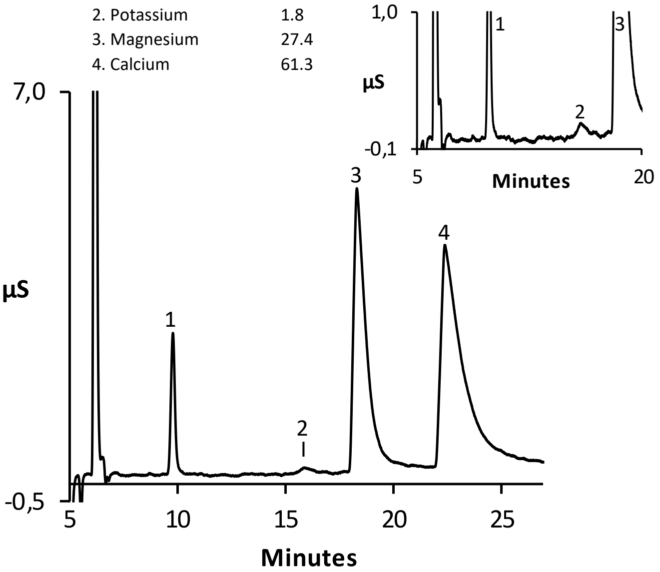

Figure 5. Determination of cations in diluted (1:1) mineral water 1 using the Sykam C05.

Column: Sykam C07 (200 x 4.0 mm) and Sykam CGC-03 (50 x 4.6 mm)
Eluent: 2.0 mM Oxalic acid, 3.5 mM 2,6-Pyridine-dicarboxylic acid
Flow Rate: 1.0 mL/min
Inj. Vol.: 10 µL
Detection: Non-suppressed Conductivity
Peaks: 1. Lithium < MRL
2. Sodium 27.8 mg/L
2. Potassium 1.9
3. Calcium 33.6
4. Magnesium 11.4

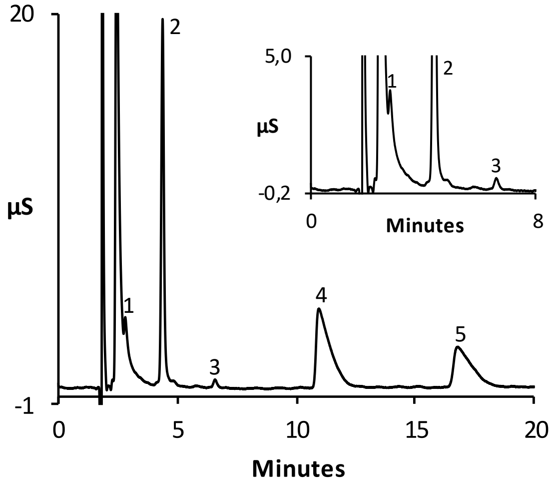

Figure 6. Determination of cations in diluted (1:1) drinking water (Straubing) using the Sykam C07.

Column: Sykam C07 (200 x 4.0 mm) and Sykam CGC-03 (50 x 4.6 mm)
Eluent: 2.0 mM Oxalic acid, 3.5 mM 2,6-Pyridine-dicarboxylic acid
Flow Rate: 1.0 mL/min
Inj. Vol.: 10 µL
Detection: Non-suppressed Conductivity
Peaks: 1. Sodium 14.7 mg/L
2. Potassium 3.0
3. Calcium 22.5
4. Magnesium 7.2

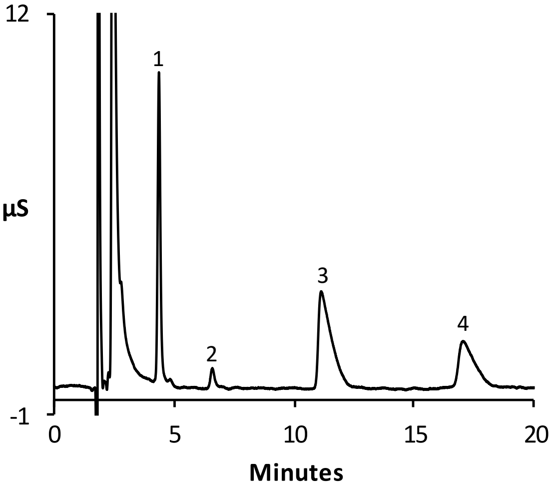

Figure 7. Determination of cations in diluted (1:1) lake water using the Sykam C07.

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. The 100% cation calibration standard was employed as check standard and for evaluation, the peak areas of each ion in the calibration standard and the check standard were directly compared to each other. During the validation using the Sykam C05, the check standards did not differ by more than 4.0% from the corresponding cation calibration standard, while the largest deviation from the corresponding calibration standard was 8.1% during the validation with the Sykam C07. In most cases the difference was less than 5%.

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 11 and 12 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 concentrations, which were found in the unfortified sample for the respective ions. If the overall content of an ion after fortification was above the highest calibration level, the samples were not spiked with the respective ion. The minimum fortification level for analytes, which 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 throughout the samples analyzed during the validation (Laboratory Fortified Blank, LFB). Table 13 summarizes the recoveries found in the Laboratory Fortified Blank for both validations.

Table 11. Recovery Data from fortified Drinking and Natural Water Samples using the Sykam C05.

Analyte	Drinking Water Straubing		Drinking Water Hamlar		Mineral Water 1 (Diluted 1:1)	
	Amount added (mg/L)	Recovery (%)	Amount added (mg/L)	Recovery (%)	Amount added (mg/L)	Recovery (%)
Lithium	0.4	96.0	0.2	101.0	0.2	90.0
Sodium	–	–	6	105.2	6	100.8
Ammonium	1	87.0	1	92.1	1	103.4
Potassium	4	105.9	4	98.3	4	92.1
Magnesium	15	102.1	15	101.9	–	–
Calcium	–	–	–	–	–	–
Analyte	**Mineral Water 2**		**Stream Water Windach**		**Lake Water Eresing**	
	Amount added (mg/L)	Recovery (%)	Amount added (mg/L)	Recovery (%)	Amount added (mg/L)	Recovery (%)
Lithium	0.2	107.0	0.2	103.5	0.2	94.0
Sodium	15	102.4	5	101.2	20	103.5
Ammonium	1	100.7	1	104.6	1	100.6
Potassium	8	101.3	4	93.3	4	112.8
Magnesium	10	93.2	15	94.7	10	110.1
Calcium	15	95.6	–	–	–	–

Table 12. Recovery Data from fortified Drinking and Natural Water Samples using the Sykam C07.

Analyte	Drinking Water Straubing (Diluted 1:1)		Drinking Water Hamlar (Diluted 1:1)		Mineral Water 1 (Diluted 1:2)	
	Amount added (mg/L)	Recovery (%)	Amount added (mg/L)	Recovery (%)	Amount added (mg/L)	Recovery (%)
Lithium	0.4	106.3	0.2	62.5	0.2	91.6
Sodium	–	–	6	94.5	6	118.9
Ammonium	1	94.5	1	133.4	1	111.2
Potassium	4	114.5	4	91.6	4	104.3
Magnesium	15	105.9	15	88.1	–	–
Calcium	–	–	–	–	–	–
Analyte	**Mineral Water 2**		**Stream Water Windach (Diluted 1:1)**		**Lake Water Eresing (Diluted 1:1)**	
	Amount added (mg/L)	Recovery (%)	Amount added (mg/L)	Recovery (%)	Amount added (mg/L)	Recovery (%)
Lithium	0.2	59.6	0.2	91.5	0.2	94.5
Sodium	15	105.6	5	111.3	20	117.9
Ammonium	1	97.9	1	116.1	1	113.1
Potassium	8	98.6	4	92.5	4	113.3
Magnesium	10	98.4	15	108.5	10	136.5
Calcium	15	87.6	–	–	–	–

Table 13. Recovery Data of the Laboratory Fortified Blank (LFB).

Analyte	Sykam C05		Sykam C07	
	Amount added (mg/L)	Recovery (%)	Amount added (mg/L)	Recovery (%)
Lithium	0.4	102.0	0.4	87.8
Sodium	20	99.6	20	101.9
Ammonium	1	111.0	1	100.9
Potassium	8	89.0	8	103.8
Magnesium	15	92.6	15	92.4
Calcium	15	86.2	15	80.9

The recoveries in the LFB range from 86–111% for the Sykam C05 and 80–104% for the Sykam C07 respectively. Using the Sykam C05 good recoveries of the cations of 87–113% were obtained. With the Sykam C07 mostly good recoveries between 87–119% were found. The recovery of lithium was low in two of the water samples (drinking water Hamlar, 63%; mineral water 2, 60%), while the recoveries of ammonium in drinking water from Hamlar (133%) and magnesium in the lake water sample (137%) were quite high.

Column:	Sykam C05 (250 x 8.0 mm) and Sykam CGC-05 (20 x 8.0 mm)
Eluent:	2.0 mM Methanesulfonic acid, 1.5 mM Oxalic acid, 60 mg/L 18-Crown-6 ether
Flow Rate:	1.5 mL/min
Inj. Vol.:	10 µL
Detection:	Non-suppressed Conductivity

Peaks:			
	1. Lithium	–	0.21 mg/L
	2. Sodium	9.8	14.6
	3. Ammonium	–	1.0
	4. Potassium	2.7	6.3
	5. Magnesium	27.8	41.3
	6. Calcium	(102.8)	96.8

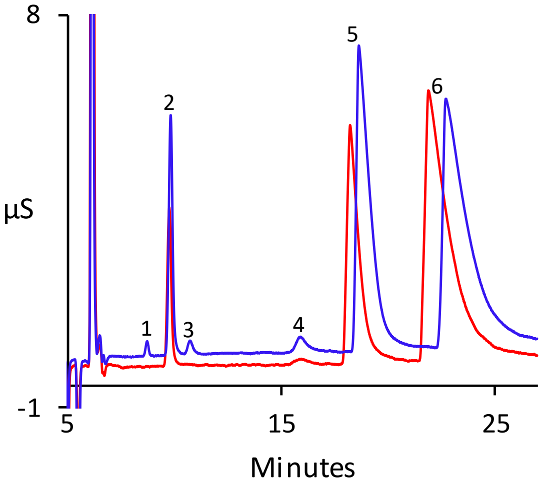

Figure 8. Determination of cations in spiked (blue) and unspiked (red) water samples of stream water using the Sykam C05.

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

Peaks:			
	1. Lithium	–	0.19 mg/L
	2. Sodium	12.3	27.5
	3. Ammonium	–	1.0
	4. Potassium	6.4	13.9
	5. Calcium	10.2	22.8
	6. Magnesium	8.4	17.9

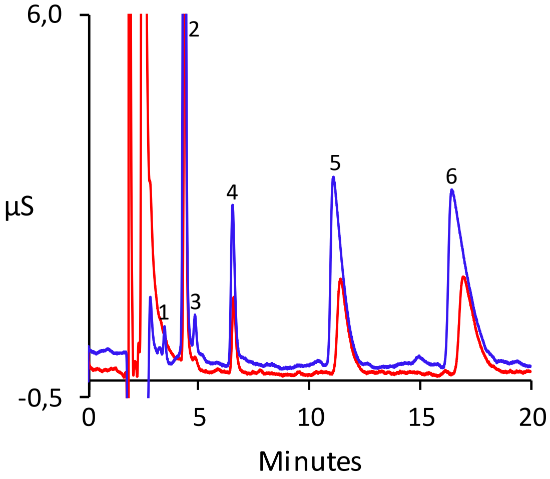

Figure 9. Determination of cations in spiked (blue) and unspiked (red) water samples of mineral water 2 using the Sykam C07.

Summary

The Sykam C05 and C07 columns provide suitable performance for the determination of inorganic cations and ammonium in natural and drinking waters, as outlined in ASTM D6919 and EN ISO 14911. This was shown by a full method validation with respect to all specifications given in the mentioned guidelines concerning the determination of method detection limits, resolution, linearity and precision. Good recovery data for the fortified sample matrices as well as for the fortified blank were found under the described chromatographic conditions. The Sykam C05, as well as the Sykam C07 reveal a high resolution for all examined standard cations, making them suitable for the analyses of complex matrices or large concentration differences between closely eluting peak pairs. The higher capacity of the Sykam C05 makes it a good choice for the analysis of samples containing relatively high amounts of cations, while the Sykam C07 is the best choice to analyze low concentrations. If shorter analysis times are preferred, the Sykam C07 should be used.

References

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

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

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

[4] *Official Journal of the European Communities*: Directive 2000/60/EC of the European Parliament and of the Council

of 23 October 2000 establishing a framework for Community action in the field of water policy.

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

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

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

[8] 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.

[9] 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

[10] 40 CFR Appendix -B-to-Part-136 – Definition and Procedure for the Determination of the Method Detection Limit – Revision 2.

[11] 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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