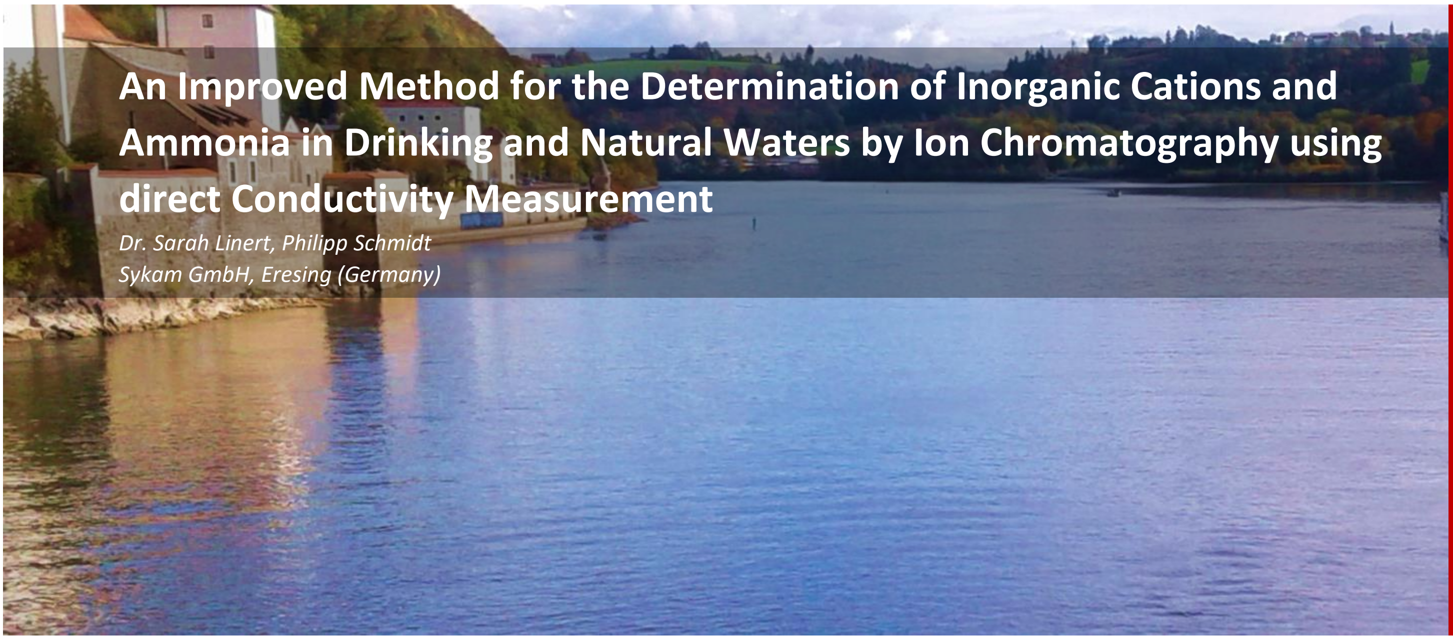

An Improved Method for the Determination of Inorganic Cations and Ammonia in Drinking and Natural Waters by Ion Chromatography using direct Conductivity Measurement

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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 by the Safe Drinking Water Act (SDWA),[3] which is meant to ensure 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 and aims 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) 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., common cations, present in drinking and natural waters, are not considered primary contaminants, but in the EU, they are regulated and monitored as well as reported by most suppliers. 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 update “Sykam AU14” describes the determination of inorganic cations and ammonium in drinking and natural waters by IC using direct conductivity measurement.

In our Application Note AN05 a method using the Sykam C07 with CGC-07 guard column was presented. For the new method described herein another eluent is used for this method to reduce the tailing of the injection peak and allow easier integration of the lithium peak. 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 system. The column Sykam C07 (200 x 4.0 mm) was used for the method validation and the validation results are discussed.

The method for cation determination described within this application update AU14 can also be used as cation determination method for simultaneous determination of anions and cations instead of the method described in application note AN03.

Equipment

Application update Sykam AU14 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 standards and reagents for eluent preparation 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)
- Lithium standard solution (traceable to SRM from NIST, $LiNO_3$ in 0.5 mol/L HNO_3, 1000 mg/L Li, Certipur®), Merck (1.70223)
- Sodium standard solution (traceable to SRM from NIST, $NaNO_3$ in H_2O, 1000 mg/L Na, Certipur®), Merck (1.19507)
- Ammonium standard solution (traceable to SRM from NIST, NH_4Cl in H_2O, 1000 mg/L NH_4, Certipur®), Merck (1.19812)
- Potassium standard solution (traceable to SRM from NIST, KNO_3 in 0.5 mol/L HNO_3, 1000 mg/L K, Certipur®), Merck (1.70230)
- Calcium standard solution (traceable to SRM from NIST, $Ca(NO_3)_2$ in 0.5 mol/L HNO_3, 1000 mg/L Ca, Certipur®), Merck (1.19778)
- Magnesium standard solution (traceable to SRM from NIST, $Mg(NO_3)_2$ in 0.5 mol/L HNO_3, 1000 mg/L Mg, Certipur®), Merck (1.19788)

If the 1000 mg/L standard solutions are freshly prepared, we recommend the use of the following analytical or ACS reagent grade chemicals. Alternatively, other chemicals of comparable or better purity can be used. Anhydrous salts should be used for the preparation of standard solutions, if possible, since they can be dried in a vacuum oven if necessary. We recommend the use of 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 (Milbertshofen, Munich)
2	Drinking Water (Penzberg)
3	Mineral Water 1
4	Mineral Water 2
5	River Water (Lech)
6	Lake Water (Untermeitingen)

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. Two drinking water samples were collected as tap water from two different municipal water suppliers in Milbertshofen (Munich) and Penzberg. The remaining two drinking water samples were commercially available mineral waters from companies, that obtain their water from natural ground water sources. The river water was collected from the Lech near Pitzling and the lake water was collected from a ground water fed pond near Untermeitingen. All samples were collected in 1000 mL PE-bottles with screw caps, and stored at 4 °C immediately after collection.

Chromatographic Conditions

Columns:	Sykam C07 (200 x 4.0 mm), Analytical column Sykam CGC-07 (50 x 4.0 mm), Guard column
Eluent:	5.0 mM Methanesulfonic acid
Flow Rate:	1.0 mL/min
Run Time:	23 min
Temperature:	35 °C
Injection Volume:	10 µL (full loop)
Detection:	Non-suppressed Conductivity (Inverted Signal)
Backpressure:	63 bar (914 psi)
Base Conductivity:	1230 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 this method uses non-suppressed conductivity detection, the signals need 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 certain cations do not 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 many 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. Therefore, standard stock solutions used for this method validation were self-prepared from the corresponding salts as described above.

For the estimation of the method detection limits of the cations, a series of mixed standards at the following concentrations was prepared: 1000, 500, 200, 100, 50, 20, 10, 5, 2 and 1 µg/L of each cation. These standards were prepared from a mixed standard with a concentration of 1 mg/L per cation. The MDL estimation was repeated at a higher injection volume of 100 µL. The concentrations of the standards prepared for the estimation of the detection limit at 100 µL injection volume were 500, 200, 100, 50, 20, 10, 5, 2, 1 and 0.5 µg/L of each cation.

Table 3 lists the concentration of the standards prepared to calculate the method detection limits (MDL_S) at 10 and 100 µL injection volume respectively, as well as the concentration of the Quality Control Sample (QCS), which is 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, ten calibration levels of a mixed cation standard were injected. The concentration levels were 0.1, 0.2, 0.5, 1, 2, 5, 10, 20, 50 and 100 mg/L for all standard cations except lithium, which is usually only present in low concentrations in water samples. Therefore, lithium was calibrated over a smaller calibration range of 0.02–20 mg/L All concentration levels were prepared from the 1000 mg/L standard stock solutions.

Table 3. Concentrations of MDL_S and QCS.

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)
Lithium	100	15	2
Sodium	500	30	15
Ammonium	500	30	5
Potassium	1500	200	10
Magnesium	1500	150	20
Calcium	1500	300	40

To assess the performance of the chromatographic system, an External Control Sample (ECS), with the same composition as the QCS is prepared. 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.

Eluent solution

For the chromatographic system discussed here, the following eluent is prepared:

5.0 mM methanesulfonic acid – Add 649.6 µL methanesulfonic acid 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).

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 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 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 must 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 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] ensuring that all requirements of these methods regarding quality control parameters are met. These methods state that optional columns and varying chromatographic conditions may be used to improve separation or lower the costs of measurements. Here, the Sykam C07 column with CGC-07 guard column and the Sykam S152-AG IC system were used for the validation, applying the chromatographic conditions listed above. The following quality control parameters were tested:

- 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
- Assessment of 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.

Table 4. Column performance parameters of the Sykam C07 (mixed cation standard) at the chromatographic conditions listed above.

Analyte	Amount (mg/L)	Retention Time (min)	Resolution R	Peak Symmetry
Lithium	0.4	3.36	–	1.05
Sodium	10	4.22	4.10	1.08
Ammonium	2	4.87	2.57	1.32
Potassium	4	6.81	5.69	1.23
Magnesium	6	13.23	5.47	1.11
Calcium	10	18.85	2.85	1.21

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.

The peak resolution is R >1.3 for all standard cations (Table 4), as required in EN ISO 14911,[9] which allows exact integration of peak areas, since all peaks are baseline-separated. The resolution of sodium and ammonium is the most critical resolution, as real samples often contain low amounts of ammonium in presence of high concentrations of sodium. Therefore, a higher resolution leads to improve detection limits of ammonium. Compared to the method described in AN05 the resolution of ammonium in AU14 is increased. The resolutions of sodium and potassium are slightly lower compared to AN05, but still very high, with values of 4.10 and 5.69 respectively. The resolution of magnesium and calcium cannot be compared directly, as the elution of these two analytes was reversed in the AN05 method, due to the presence of 2,6-pyridine-dicarboxylic acid.

Column: Sykam C07 (200 x 4.0 mm) and Sykam CGC-07 (50 x 4.0 mm)
Eluent: 5.0 mM methanesulfonic 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. Magnesium 6.0
6. Calcium 10.0

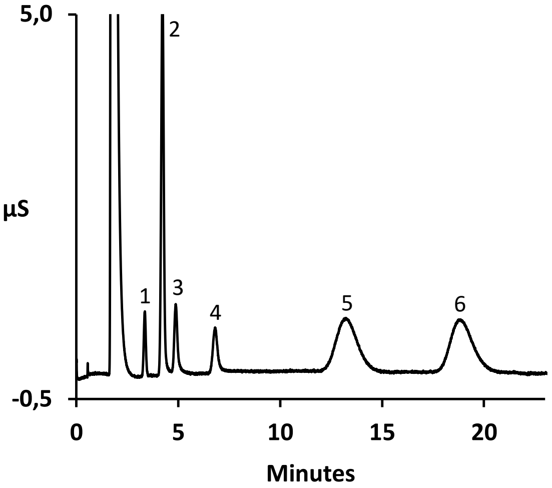

Figure 2. Separation of a mixed inorganic cation standard.

Method Detection Limits MDL_S and MDL_B

First, the method detection limits based on sample injection (MDL_S) were estimated. Ten mixed cation standards with concentrations of 1000, 500, 200, 100, 50, 20, 10, 5, 2 and 1 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 standard (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 $MDL_S = t \times SD$, 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. [10] The thus obtained method detection limits are listed in table 5. 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. The MDLs of all cations is significantly lower than for the method described in AN05, especially the MDLs for potassium and calcium.

The Sykam C07 column exhibits 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 alkaline earth 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 alkaline earth metals and potassium. If the samples are known to contain only small amounts of 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 method detection limits were also repeated for a 100 µL instead of a 10 µL sample loop. The same chromatographic conditions as mentioned above were applied and full loop injections were performed. For the estimation of the method detection limits at 100 µL injection volume, ten mixed cation standards with the following concentrations of each individual cation were analyzed: 500, 200, 100, 50, 20, 10, 5, 2, 1 and 0.5 µg/L. The concentrations of the corresponding MDL$_S$-Calculation standard are listed in table 3 and the obtained method detection limits are listed in table 5. As expected, the calculated method detection limits are significantly lower for a larger injection volume. For all cations an MDL of less than 100 µg/L was obtained. For the early eluting analytes lithium, sodium and ammonium, the method detection limits were <10 µg/L. Like for the injection volume of 10 µL, the method detection limits obtained using 100 µL injection volume were lower than for those obtained using the AN05 method.

Table 5. Linearity, MDL$_S$, retention time and peak area precision.

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	0.02–20	1.0000	14.5	1.3	0.19	0.59
Sodium	0.1–100	1.0000	35.8	3.7	0.16	0.41
Ammonium	0.1–100	1.0000	33.0	3.3	0.14	1.71
Potassium	0.2–100	1.0000	72.7	22.6	0.10	1.29
Magnesium	0.2–100	1.0000	127.5	24.9	0.16	0.85
Calcium	0.5–100	1.0000	86.2	63.5	0.09	1.19

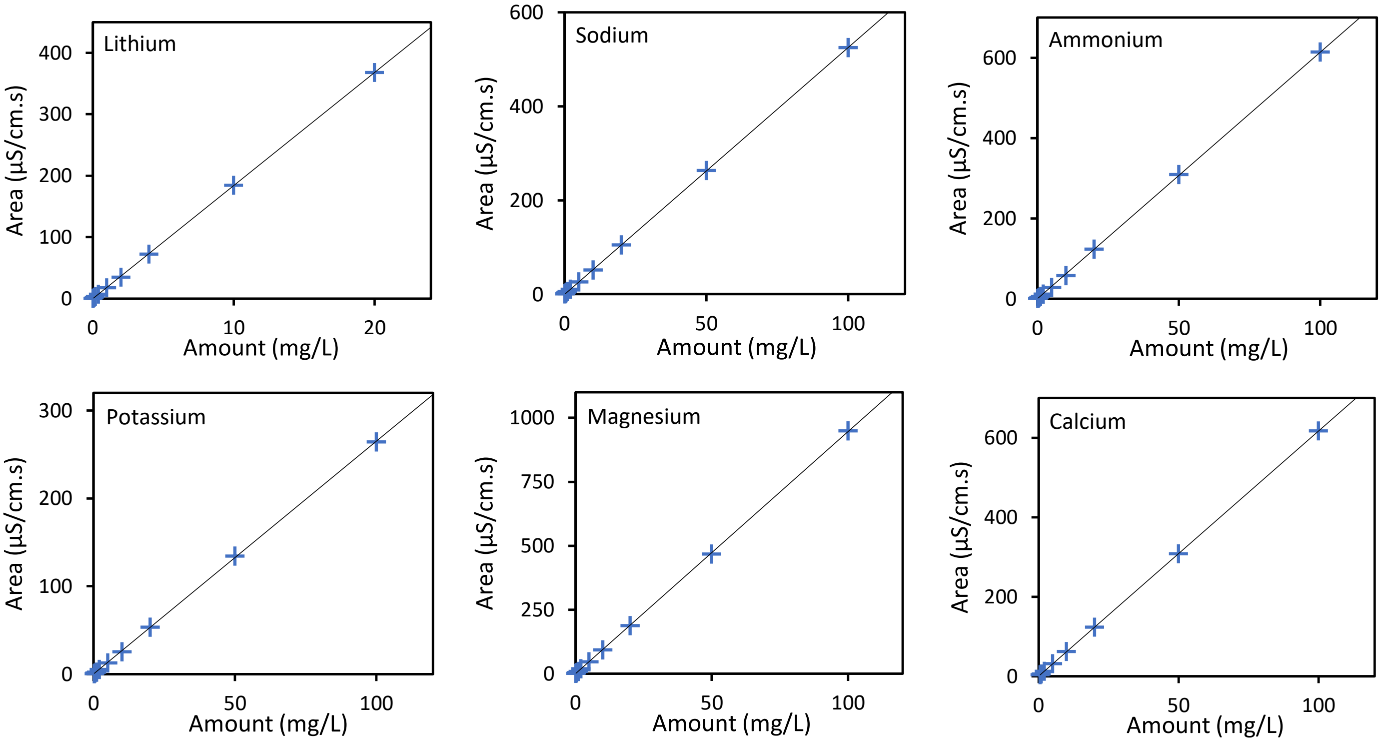

Figure 3. Calibration plots of the standard cations indicating the LCR used for analysis of the samples

Linearity (LCR)

For the assessment of the linear calibration range, mixed cation standards at ten calibration levels were injected. The standards contained 0.1, 0.2, 0.5, 1, 2, 5, 10, 20, 50 and 100 mg/L of all standard cations, except for lithium, which was calibrated over a smaller range of 0.02–20 mg/L. Figure 3 shows the linear calibration plots for all cations. Calibration points that are below the calculated MDL$_S$ are omitted.

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 0.02–20 mg/L.

In table 5 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. Due to the use of self-prepared standard stock solutions with no added nitric acid, the cations could be calibrated over a wider range than in AN05. Except for lithium, all cations could be calibrated to lower concentrations than in AN05, due to the lower MDLs. The correlation factors are higher than those obtained for the method described in AN05 and are all >0.999.

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 cations in the QCS are similar to those found in the field samples. The concentrations are listed in table 3. Table 5 lists the results of the Relative Standard Deviation (RSD) of retention time and peak area, after seven replicate injections of the QCS. For all investigated ions, the retention time RSD is well below 1.0% and the peak area RSD was found to be less than 2.0%. For some of the cations, the retention time RSD is slightly higher than for the method described in AN05. The peak area RSD of ammonium is comparable to the AN05 method, while it is significantly lower for the other cations, especially lithium and potassium.

Table 6. Relative Percent Differences (RPD) of QCS and ECS.

Analyte	RPD (%)
Lithium	2.5
Sodium	0.9
Ammonium	1.1
Potassium	-1.9
Magnesium	5.3
Calcium	2.9

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 analysis of an External Calibration Standard (ECS). The ECS is prepared from 1000 mg/L single cation standard stock solutions, which are 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%. The RPD for magnesium and calcium are higher than for the AN05 method, but all other RPD values are lower, especially those for ammonium and potassium.

Sample Analysis

All six samples were analyzed undiluted after filtration, each as initial sample and laboratory duplicate.

Table 8 gives an overview of the analysis results for the six drinking and natural water samples, listing the mean value of the initial sample and duplicate analysis and their Relative Percent Difference (RPD).

For the analysis of real samples, only values above the Minimum Reporting Level (MRL) are listed. 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 7 gives an overview of the MRLs for each cation based on the applied linear calibration range and the calculated MDLs.

Table 7. Minimum Reporting Levels based on the LCR and MDL.

Analyte	MRL (mg/L)
Lithium	0.02
Sodium	0.1
Ammonium	0.1
Potassium	0.2
Magnesium	0.2
Calcium	0.5

Lithium and ammonium were not detected in any of the drinking and natural water samples. Potassium was found only in low concentrations between 0.7–7.7 mg/L. The detected concentrations of sodium and magnesium range from 7.8–17.2 mg/L and 3.6–35.4 mg/L respectively. The amounts of calcium in the drinking and natural waters vary over a range of 43.6–88.3 mg/L. All values are within the typical ranges that are usually found for drinking and natural water samples.

Table 8. Analysis results (mg/L) and RPD (%) of duplicate analyses of the water samples.

Analyte	Drinking Water Milbertshofen	Drinking Water Penzberg	Mineral Water 1
Lithium	n.d.	n.d.	n.d.
Sodium	7.8 (0.0)	7.9 (-2.3)	12.5 (-0.2)
Ammonium	n.d.	n.d.	n.d.
Potassium	1.5 (-0.2)	1.2 (0.7)	2.2 (1.3)
Magnesium	20.2 (-0.3)	25.7 (-2.2)	35.4 (0.2)
Calcium	75.0 (0.2)	88.3 (-1.7)	81.8 (-1.4)
Analyte	**Mineral Water 2**	**River Water Lech**	**Lake Water Untermeitingen**
Lithium	n.d.	n.d.	n.d.
Sodium	17.2 (-0.1)	2.9 (0.8)	16.5 (0.0)
Ammonium	n.d.	n.d.	n.d.
Potassium	2.1 (1.2)	0.7 (1.0)	7.7 (-2.2)
Magnesium	3.6 (-0.4)	13.8 (-0.8)	20.6 (-0.8)
Calcium	46.7 (-0.9)	43.6 (-1.0)	60.8 (-0.4)

The values found in the laboratory duplicates do not differ significantly from the respective initial samples (RPD <3%), 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 results is very high.

Table 9 summarizes the 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 1 reported by the supplier are slightly lower than those found during this validation. For mineral water 2 the determined values correspond well with the analysis results given by the supplier as shown in table 9.

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
Sodium	12.5	8.8	17.2	16.4
Potassium	2.2	1.8	2.1	2.0
Magnesium	35.4	30.5	3.6	3.6
Calcium	81.8	79.9	46.7	47.0

Column: Sykam C07 (200 x 4.0 mm) and Sykam CGC-07 (50 x 4.0 mm)
Eluent: 5.0 mM methanesulfonic acid
Flow Rate: 1.0 mL/min
Inj. Vol.: 10 µL
Detection: Non-suppressed Conductivity
Peaks: 1. Sodium 7.8 mg/L
2. Potassium 1.5
3. Magnesium 20.2
4. Calcium 75.0

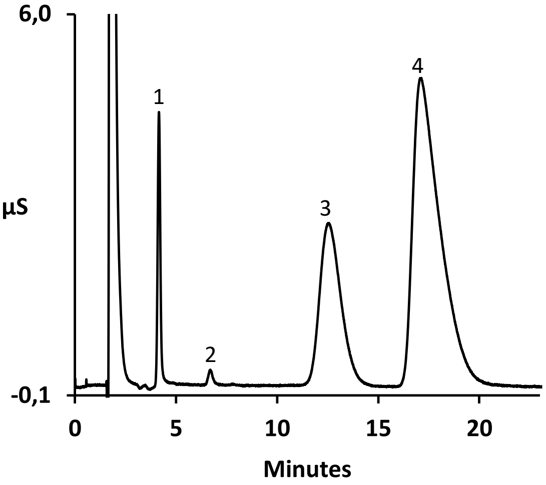

Figure 6. Determination of cations in drinking water (Milbertshofen).

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 10% cation calibration standard was used as check standard and for evaluation. The peak areas of each ion in the calibration standard and the check standards were directly compared to each other. During the validation, the check standards did not differ by more than 4.0% from the corresponding cation calibration standard. In most cases the difference was less than 2.0%.

Column: Sykam C07 (200 x 4.0 mm) and Sykam CGC-07 (50 x 4.0 mm)
Eluent: 5.0 mM methanesulfonic acid
Flow Rate: 1.0 mL/min
Inj. Vol.: 10 µL
Detection: Non-suppressed Conductivity
Peaks: 1. Sodium 12.5 mg/L
2. Potassium 2.2
3. Magnesium 35.4
4. Calcium 81.8

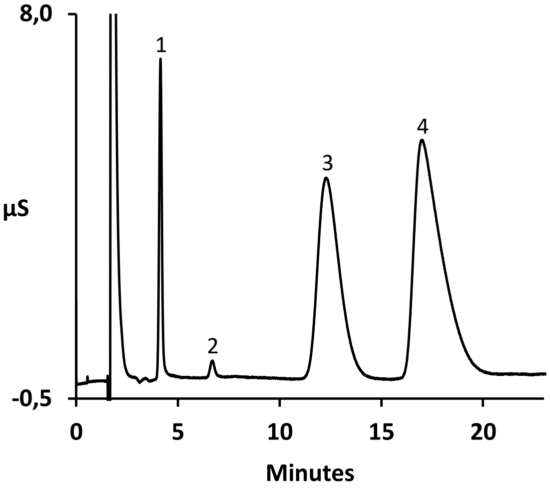

Figure 7. Determination of cations in mineral water 1.

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). Table 11 lists the obtained recovery results for single-operator data for the standard inorganic cations 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 would have been 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 spiked into the samples (Laboratory Fortified Blank, LFB). Table 10 summarizes the recoveries found in the Laboratory Fortified Blank

Table 10. Recovery Data of the Laboratory Fortified Blank (LFB).

Analyte	Amount added (mg/L)	Recovery (%)
Lithium	0.5	99.6
Sodium	20	97.1
Ammonium	1	100.0
Potassium	10	99.8
Magnesium	40	100.2
Calcium	50	96.4

The recoveries in the LFB range from 96-101% while the recoveries in the fortified samples are within the range of 94–110%. These are very good recoveries for all cations and well within the required range of ±15%.

Table 11. Recovery Data from fortified Drinking and Natural Water Samples using the Sykam C07.

Analyte	Drinking Water Milbertshofen		Drinking Water Penzberg		Mineral Water 1	
	Amount added (mg/L)	Recovery (%)	Amount added (mg/L)	Recovery (%)	Amount added (mg/L)	Recovery (%)
Lithium	0.5	107.4	0.5	109.4	0.5	106.2
Sodium	10	95.3	10	96.6	15	96.8
Ammonium	1	103.6	1	103.6	1	107.7
Potassium	2	102.8	2	96.9	5	104.4
Magnesium	25	100.5	30	101.2	40	100.4
Calcium	–	–	–	–	–	–

Analyte	Mineral Water 2		River Water Lech		Lake Water Untermeitingen	
	Amount added (mg/L)	Recovery (%)	Amount added (mg/L)	Recovery (%)	Amount added (mg/L)	Recovery (%)
Lithium	0.5	101.2	0.5	103.0	0.5	98.4
Sodium	20	94.7	5	97.0	20	95.7
Ammonium	1	100.2	1	102.4	1	101.3
Potassium	5	101.7	2	94.1	10	100.9
Magnesium	5	101.5	15	102.1	25	99.5
Calcium	50	99.9	50	97.9	–	–

Column: Sykam C07 (200 x 4.0 mm) and Sykam CGC-07 (50 x 4.0 mm)
Eluent: 5.0 mM methanesulfonic acid
Flow Rate: 1.0 mL/min
Inj. Vol.: 10 µL
Detection: Non-suppressed Conductivity

Peaks:			
	1. Lithium	–	0.52 mg/L
	2. Sodium	2.9	7.6
	3. Ammonium	–	1.0
	4. Potassium	0.68	2.5
	5. Magnesium	13.8	28.1
	6. Calcium	43.6	89.4

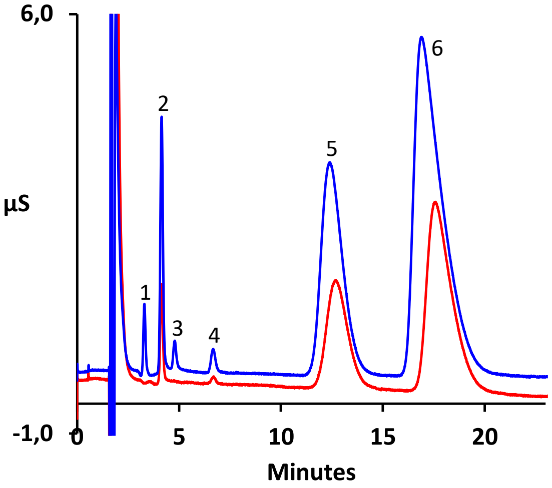

Figure 9. Determination of cations in spiked (blue) and unspiked (red) samples of river water.

Summary

The Sykam C07 column provides 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. Very good recovery data for the fortified sample matrices, as well as the fortified blank, were found under the described chromatographic conditions. The Sykam C07 shows a high resolution for all examined standard cations, making it suitable for the analysis of complex matrices and large concentration differences between closely eluting cation pairs. The improved method described within this application update AU14 provides lower detection limits compared to the previous method described in application note AN05 and allows the determination of standard cations over a wider calibration range. The sodium/ammonium resolution, as well as the precision of the method, are also improved.

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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