

# Determination of Inorganic Cations and Ammonia in Drinking and Natural Waters by Ion Chromatography using Electrochemical Suppression

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## Introduction

To ensure that human health is not affected by pollution from industrial and other human sources the quality of drinking water is monitored all over the world. In the European Union, the Drinking Water Directive (DWD) 98/83/EC<sup>[1]</sup> from 1998, with its latest version 2020/2184<sup>[2]</sup> 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),<sup>[3]</sup> which ensures the integrity and safety of drinking waters. Additionally, the European Union established the Water Framework Directive 2000/60/EC<sup>[4]</sup> in October 2000, which aims to secure the quality of groundwater, inland surface waters, transitional waters and coastal waters, in order to protect and enhance the status of aquatic ecosystems and prevent their further deterioration. The respective primary federal law in the United States is the Clean Water Act (CWA).<sup>[5]</sup> The content of specific chemicals is regulated by Maximum Contaminant Levels (MCL) e.g. under the EU Drinking Water Directive (DWD)<sup>[2]</sup> or the U.S. National Primary and Secondary Drinking Water Standards (NPDWS/NSDWS).<sup>[6]</sup> 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, as well as monitored and reported by most suppliers. Ammonium is of special interest, since it dissociates to ammonia in water, depending on temperature and pH value. The degree of this dissociation determines its toxicity to aquatic life.<sup>[7]</sup> Furthermore, among the earth alkaline metals, calcium and magnesium are determined to measure the hardness of water, while Strontium is not regulated in the U.S. or the EU and barium is regulated as a primary contaminant with an MCL of 2 mg/L in the U.S. In the EU, barium is not regulated.<sup>[6]</sup>

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 to the determination of cations in

natural and drinking waters. The methods for analysis of cations and ammonium using IC are described in ASTM D6919<sup>[8]</sup> and EN ISO 14911.<sup>[9]</sup> ASTM D6919 covers the common cations lithium, sodium, ammonium, potassium, magnesium and calcium.<sup>[8]</sup> EN ISO 14911 also lists these cations, but furthermore includes manganese, strontium and barium.<sup>[9]</sup>

This application note "Sykam AN11" describes the determination of inorganic cations and ammonium in drinking and natural waters by IC using suppressed conductivity measurement. The methods were validated under consideration of the requirements described in the aforementioned methods for cation analysis and therefore provide an economical way to meet the testing requirements of ASTM D6919<sup>[8]</sup> and EN ISO 14911<sup>[9]</sup> using a Sykam S152+ IC system. Both methods allow the use of suppressed conductivity detection. In the S152+ IC system an electrochemical, self-regenerating suppressor is used to lower the base conductivity, reducing baseline noise, which leads to significantly lower detection limits compared to non-suppressed conductivity detection.

The columns Sykam C06 (100 x 4.6 mm) and Sykam C07 (200 x 4.0 mm) were used for the method validation and the validation results are discussed. The method validations were performed for the determination of the six common cations alongside strontium and barium.

The method for cation determination using the Sykam C07 described in this application note AN11 can also be used in place of the method for the Sykam C06 for simultaneous determination of anions and cations as described in application note AN09.

## Equipment

Application note Sykam AN11 is designed for the use of a Sykam S152-AG+ IC system with single-channel cation detection, consisting of the following components:

- S150+ Ion Chromatography Module including column oven, single-channel conductivity detector and electrochemical self-regenerating cation suppressor module
- 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.

Alternatively, instead of the S152-AG+ IC system a S153-AG+ Dual IC system 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  $\mu\text{S}/\text{cm}$  conductivity (10  $\text{k}\Omega/\text{cm}$  resistivity) or better
- Methanesulfonic acid ( $\text{CH}_3\text{SO}_3\text{H}$ ,  $\geq 99.0\%$ ), Sigma-Aldrich (471356)
- Lithium standard solution (traceable to SRM from NIST,  $\text{LiNO}_3$  in 0.5 mol/L  $\text{HNO}_3$ , 1000 mg/L Li, Certipur®), Merck (1.70223)
- Sodium standard solution (traceable to SRM from NIST,  $\text{NaNO}_3$  in  $\text{H}_2\text{O}$ , 1000 mg/L Na, Certipur®), Merck (1.19507)
- Ammonium standard solution (traceable to SRM from NIST,  $\text{NH}_4\text{Cl}$  in  $\text{H}_2\text{O}$ , 1000 mg/L  $\text{NH}_4$ , Certipur®), Merck (1.19812)
- Potassium standard solution (traceable to SRM from NIST,  $\text{KNO}_3$  in 0.5 mol/L  $\text{HNO}_3$ , 1000 mg/L K, Certipur®), Merck (1.70230)
- Calcium standard solution (traceable to SRM from NIST,  $\text{Ca}(\text{NO}_3)_2$  in 0.5 mol/L  $\text{HNO}_3$ , 1000 mg/L Ca, Certipur®), Merck (1.19778)
- Magnesium standard solution (traceable to SRM from NIST,  $\text{Mg}(\text{NO}_3)_2$  in 0.5 mol/L  $\text{HNO}_3$ , 1000 mg/L Mg, Certipur®), Merck (1.19788)
- Strontium standard solution (traceable to SRM from NIST,  $\text{Sr}(\text{NO}_3)_2$  in 0.5 mol/L  $\text{HNO}_3$ , 1000 mg/L Sr, Certipur®), Merck (1.19799)
- Barium standard solution (traceable to SRM from NIST,  $\text{Ba}(\text{NO}_3)_2$  in 0.5 mol/L  $\text{HNO}_3$ , 1000 mg/L Ba, Certipur®), Merck (1.19774)

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 ( $\text{LiNO}_3$ , anhydrous, extra pure, SLR), Fisher Chemical (10568620)
- Sodium nitrate ( $\text{NaNO}_3$ , for analysis EMSURE, ACS, ISO, Reag. Ph Eur), Merck (1.06537)
- Ammonium chloride ( $\text{NH}_4\text{Cl}$ , Suprapur®), Merck (1.01143)
- Potassium nitrate ( $\text{KNO}_3$ , ACS reagent,  $\geq 99.0\%$ ), Sigma-Aldrich (221295)
- Calcium nitrate tetrahydrate ( $\text{Ca}(\text{NO}_3)_2 \cdot 4 \text{H}_2\text{O}$ , for analysis EMSURE, ACS, ISO, Reag. Ph Eur), Merck (1.02121)
- Magnesium nitrate hexahydrate ( $\text{Mg}(\text{NO}_3)_2 \cdot 6 \text{H}_2\text{O}$ , ACS reagent, 99%), Sigma-Aldrich (237175)
- Strontium nitrate ( $\text{Sr}(\text{NO}_3)_2$ , ACS reagent,  $\geq 99.0\%$ ), Sigma-Aldrich (243426)
- Barium nitrate ( $\text{Ba}(\text{NO}_3)_2$ , ACS reagent,  $\geq 99\%$ ), Sigma-Aldrich (217581)

## Samples

For the method validation, six water samples were analyzed.

Table 1. List of analyzed samples.

No.	Name
1	Drinking Water (Karlsfeld)
2	Drinking Water (Wörthsee)
3	Mineral Water 1
4	Mineral Water 2
5	Stream Water (Pitzling)
6	Lake Water (Graben)

All six water samples were collected in Southern Germany in the northern foothills of the Alps. Four of the samples were drinking water samples, while the remaining two samples were natural surface water samples. The two drinking water samples were collected as tap water from two different municipal water suppliers in Karlsfeld and Wörthsee. The two mineral water samples were commercially available mineral waters from companies, which obtain the water from natural groundwater sources. The stream water was collected from a stream near Pitzling and the lake water was collected from a groundwater-fed pond near Graben. 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 1 (Sykam C06)

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:	23 min, with Sr <sup>2+</sup> : 33 min, with Ba <sup>2+</sup> : 67 min
Temperature:	35 °C
Injection Volume:	10 µL (full loop)
Detection:	Suppressed Conductivity
Backpressure:	33 bar (480 psi)
Base Conductivity:	0.6 µS/cm
Noise:	<1 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:	5.0 mM Methanesulfonic acid
Flow Rate:	1.0 mL/min
Run Time:	23 min, with Sr <sup>2+</sup> : 35 min, with Ba <sup>2+</sup> : 57 min
Temperature:	35 °C
Injection Volume:	10 µL (full loop)
Detection:	Suppressed Conductivity
Backpressure:	68 bar (990 psi)
Base Conductivity:	0.5 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.

## Preparation of Solutions and Reagents

### Standard Stock Solutions (1000 mg/L)

The standard stock solutions of the six cations lithium, sodium, ammonium, potassium, calcium and magnesium as well as strontium and barium 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 one of the listed cations does 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 <sub>3</sub> )	9.933
Sodium	Sodium nitrate (NaNO <sub>3</sub> )	3.697
Ammonium	Ammonium chloride (NH <sub>4</sub> Cl)	2.965
Potassium	Potassium nitrate (KNO <sub>3</sub> )	2.586
Calcium	Calcium nitrate tetrahydrate (Ca(NO <sub>3</sub> ) <sub>2</sub> · 4 H <sub>2</sub> O)	5.892
Magnesium	Magnesium nitrate hexahydrate (Mg(NO <sub>3</sub> ) <sub>2</sub> · 6 H <sub>2</sub> O)	10.547
Strontium	Strontium nitrate (Sr(NO <sub>3</sub> ) <sub>2</sub> )	2.415
Barium	Barium nitrate (Ba(NO <sub>3</sub> ) <sub>2</sub> )	1.903

### 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 and ASTM D6919 a low pH value of the sample can interfere with analysis.<sup>[8,9]</sup> Since most of the commercially available standard stock solutions are solutions of the corresponding salts in 0.5 mol/L HNO<sub>3</sub>, they 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 C06 or C07, especially in the presence of high amounts of nitrate. Therefore, standard stock solutions used for method validation were 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 concentrations of 100, 50, 20, 10, 5, 2, 1 and 0.5 µg/L of lithium, sodium, ammonium, potassium, magnesium and calcium were prepared from 10 mg/L single standard solutions. The respective concentrations of strontium and barium were 2000, 1000, 400, 200, 100, 40, 20 and 10 µg/L.

Table 3 lists the concentrations of the standards prepared to calculate the method detection limits (MDL<sub>s</sub>) 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.

For the determination of the linear calibration range of the six standard cations, as well as strontium and barium, covering the expected concentrations of drinking and natural water samples, eleven calibration levels of a mixed cation standard were injected. The concentration levels were 0.05, 0.1, 0.2, 0.5, 1, 2, 5, 10, 20, 50 and 100 mg/L of all cations, except for lithium, which was calibrated over a smaller range of 0.01–20 mg/L. All concentration levels are prepared from the 1000 mg/L standard stock solutions.

To assess the performance of the chromatographic system, an External Control Sample (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 of salts to be used for the preparation of these standards are given in table 2.



Table 3. Concentrations of MDL<sub>s</sub>-Calculation Standard and QCS.

Analyte	MDL <sub>s</sub> Calculation Standard (µg/L)		QCS for Precision (mg/L)	
	Sykam C06	Sykam C07	Sykam C06	Sykam C07
Lithium	2	1	2	2
Sodium	10	5	15	15
Ammonium	10	5	5	5
Potassium	20	10	10	10
Magnesium	40	20	20	20
Calcium	50	20	40	40
Strontium	400	150	10	10
Barium	2000	400	10	10

### Eluent solution

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

Sykam C06/C07: 5.0 mM methanesulfonic acid – Add 649.6 µL of 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 respective eluent before slowly increasing the flow rate to the desired value. To achieve reproducible results, the system and especially the suppressor unit have to warm up and be equilibrated. For equilibration, switch on the column oven and the suppressor at the respective conditions. Apply the desired flow rate until the baseline has stabilized. The baseline noise should be <5.0 nS/cm. 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 analysis. 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<sup>[8]</sup> and EN ISO 14911,<sup>[9]</sup> ensuring that all requirements of these methods regarding quality control parameters are met. These methods state that alternative columns and varying chromatographic conditions may be used to improve separation or lower the costs of measurements. Here, the Sykam C06 and Sykam C07 columns together with 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<sub>s</sub> and MDL<sub>B</sub><sup>[10]</sup>
- Linearity (Linear Calibration Range, LCR)<sup>[11]</sup>
- 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.

The Sykam C06 is a cation exchange column based on a carboxylic acid functionalized EVB-DVB resin with a particle size of 7 µm. Figure 1 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  
 Peaks: 1. Lithium 2.0 mg/L  
 2. Sodium 15.0  
 3. Ammonium 5.0  
 4. Potassium 10.0  
 5. Magnesium 20.0  
 6. Calcium 40.0  
 7. Strontium 10.0  
 8. Barium 10.0

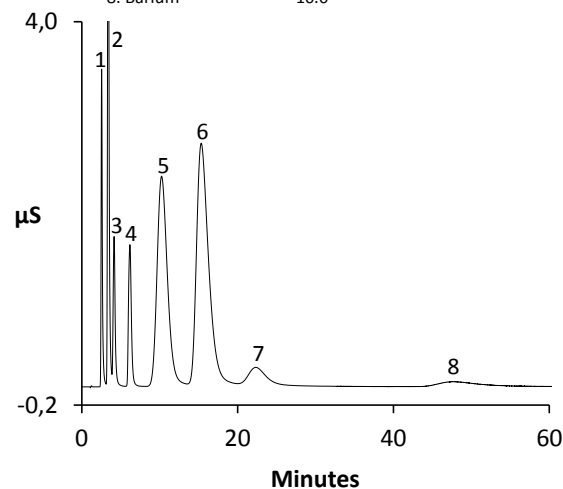


Figure 1. Separation of the QCS using the Sykam C06.

Table 4. Column performance parameters of the QCS using the Sykam C06 and Sykam C07 at the chromatographic conditions listed above.

Analyte	Retention Time (min)		Resolution R		Peak Symmetry	
	Sykam C06	Sykam C07	Sykam C06	Sykam C07	Sykam C06	Sykam C07
Lithium	2.56	3.50	–	–	1.50	1.56
Sodium	3.40	4.31	2.82	3.10	1.40	1.53
Ammonium	4.15	4.97	1.91	1.84	1.25	2.06
Potassium	6.18	6.67	3.60	3.87	1.24	1.72
Magnesium	10.24	12.92	2.65	5.09	1.29	1.36
Calcium	15.33	17.85	1.97	2.33	1.53	1.68
Strontium	22.34	23.64	1.98	2.32	1.58	1.28
Barium	47.71	41.30	3.80	4.62	1.88	1.74

The Sykam C07 is a cation exchange column based on a weak acid functionalized EVB-DVB resin with a particle size of 7 µm. Figure 2 shows the separation of an inorganic cation standard using the Sykam C07.

Column: Sykam C07 (200 x 4.0 mm) and Sykam CGC-07 (50 x 4.0 mm)  
 Eluent: 5.0 mM Methanesulfonic acid  
 Flow Rate: 1.0 mL/min  
 Inj. Vol.: 10 µL  
 Detection: Suppressed Conductivity  
 Peaks: 1. Lithium 2.0 mg/L  
 2. Sodium 15.0  
 3. Ammonium 5.0  
 4. Potassium 10.0  
 5. Magnesium 20.0  
 6. Calcium 40.0  
 7. Strontium 10.0  
 8. Barium 10.0

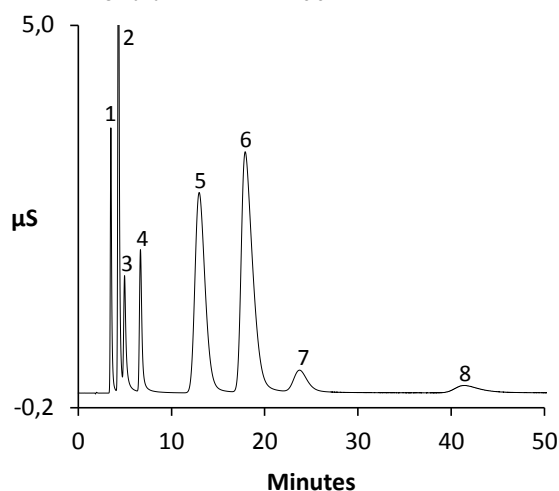


Figure 2. Separation of the QCS using the Sykam C07.

The peak resolution is  $R > 1.3$  for all standard cations (Table 4) on both columns, as required by EN ISO 14911,<sup>[9]</sup> allowing for exact integration of peak areas.

As both columns exhibit a low capacity, a low injection volume of 10 µL was used for the method validation, to allow the determination of higher concentrations of alkaline earth metals without dilution of the samples.

The retention times for all cations except for barium are slightly longer when using the Sykam C07 compared to the Sykam C06, but the retention time of barium is shorter when using the Sykam C07. The peak resolution of ammonium is better when using the Sykam C06, while the resolution for the other cations is better on the Sykam C07. The peak symmetry for all cations except strontium and barium

is better using the Sykam C06. For strontium and barium, the peak symmetry is better on the Sykam C07. Also, the peaks of the alkaline earth metals are narrower on the Sykam C07 which makes them easier to integrate. Therefore, we recommend to use the Sykam C07 for the determination of strontium and barium. If the focus is on the determination of ammonium, we recommend to use the Sykam C06, which exhibits better resolution of sodium and ammonium.

If strontium and barium are not present in the samples, which are to be determined, the run time can be shortened accordingly.

#### Method Detection Limits MDL<sub>S</sub> and MDL<sub>B</sub>

First, the method detection limits based on sample injection (MDL<sub>S</sub>) were estimated. Therefore, eight mixed cation standards with concentrations of 100, 50, 20, 10, 5, 2, 1 and 0.5 µg/L of all cations except strontium and barium were injected. The respective concentrations of strontium and barium were 2000, 1000, 400, 200, 100, 40, 20 and 10 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<sub>S</sub>-Calculation standards (Table 3). The MDL<sub>S</sub> for each ion was determined by performing seven replicate injections of the MDL<sub>S</sub>-Calculation standard. The MDL<sub>S</sub> 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<sub>S</sub>-Calculation standard for each ion.<sup>[10]</sup> The thus obtained method detection limits are listed in tables 6 and 7. In contrast to the MDL<sub>S</sub>, the MDL<sub>B</sub> 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.<sup>[10]</sup> In case of the Sykam C06, seven replicates of the LRB were analyzed with the result that none of the cations were found in any of the LRB injections. During the validation of the Sykam C07, small amounts of sodium and potassium were found in the LRB. Therefore, for these two ions the MDL<sub>B</sub> is applied instead of the MDL<sub>S</sub>. The MDL<sub>B</sub> is 1.0 µg/L for sodium and 3.0 µg/L for potassium.

The detection limits of the common cations are less than 5.0 µg/L for both columns and within a similar range. For strontium and barium, the MDLs are lower using the Sykam C07. As the peaks of the alkaline earth metals are narrower when using the Sykam C07 it is easier to integrate them and the analytes can be determined to lower concentrations.

The Sykam C07 can also be used with non-suppressed conductivity detection using the same chromatographic conditions as listed above. The respective method is described in our application update AU14. Without suppression the MDL<sub>s</sub> are in the range of 14.5 µg/L (lithium) to 127.5 µg/L (magnesium) without strontium and barium.

### Linearity (LCR)

For the assessment of the calibration range of the analyzed cations, mixed cation standards at eleven calibration levels were injected: 0.05, 0.1, 0.2, 0.5, 1, 2, 5, 10, 20, 50 and 100 mg/L of all cations, except lithium. The respective concentrations of lithium were 0.01, 0.02, 0.05, 0.1, 0.2, 0.5, 1, 2, 5, 10 and 20 mg/L. Figures 3 (Sykam C06) and 4 (Sykam C07) show the calibration plots for all cations.

All cations except for lithium and ammonium 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 0.01–20 mg/L. Ammonia is a weak base meaning that the ammonium cation can be deprotonated during suppression. Therefore, when using suppressed conductivity detection for ammonium, the calibration curve is not linear as for the alkaline and alkaline earth metals. Usually, a quadratic fit is applied for ammonium. Also, ammonium was only calibrated up to 20 mg/L since the two highest calibration points varied too much from the other calibration points. But as ammonium is not expected to be present in high concentrations in drinking and natural water samples this limited calibration range usually does not affect the determination of ammonium.

In tables 6 and 7 the calibration ranges as well as the correlation factors  $r^2$  of the fits for all ions are listed. All fits exhibit correlation factors of  $r^2 > 0.995$  as required in ASTM D6919<sup>[8]</sup> and are therefore considered very accurate.

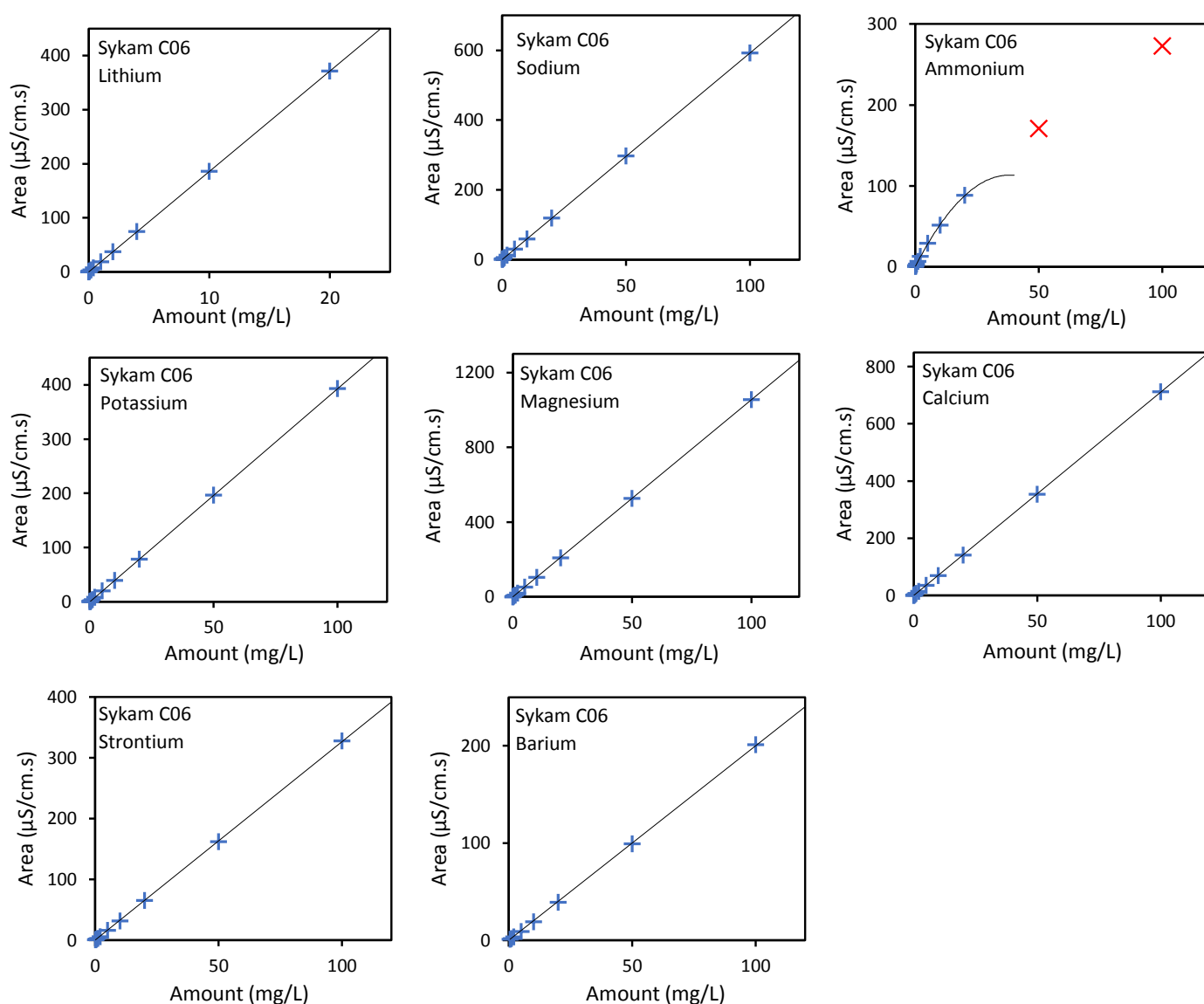


Figure 3. Calibration plots of the standard cations showing the LCR used for analysis of the samples using the Sykam C06.

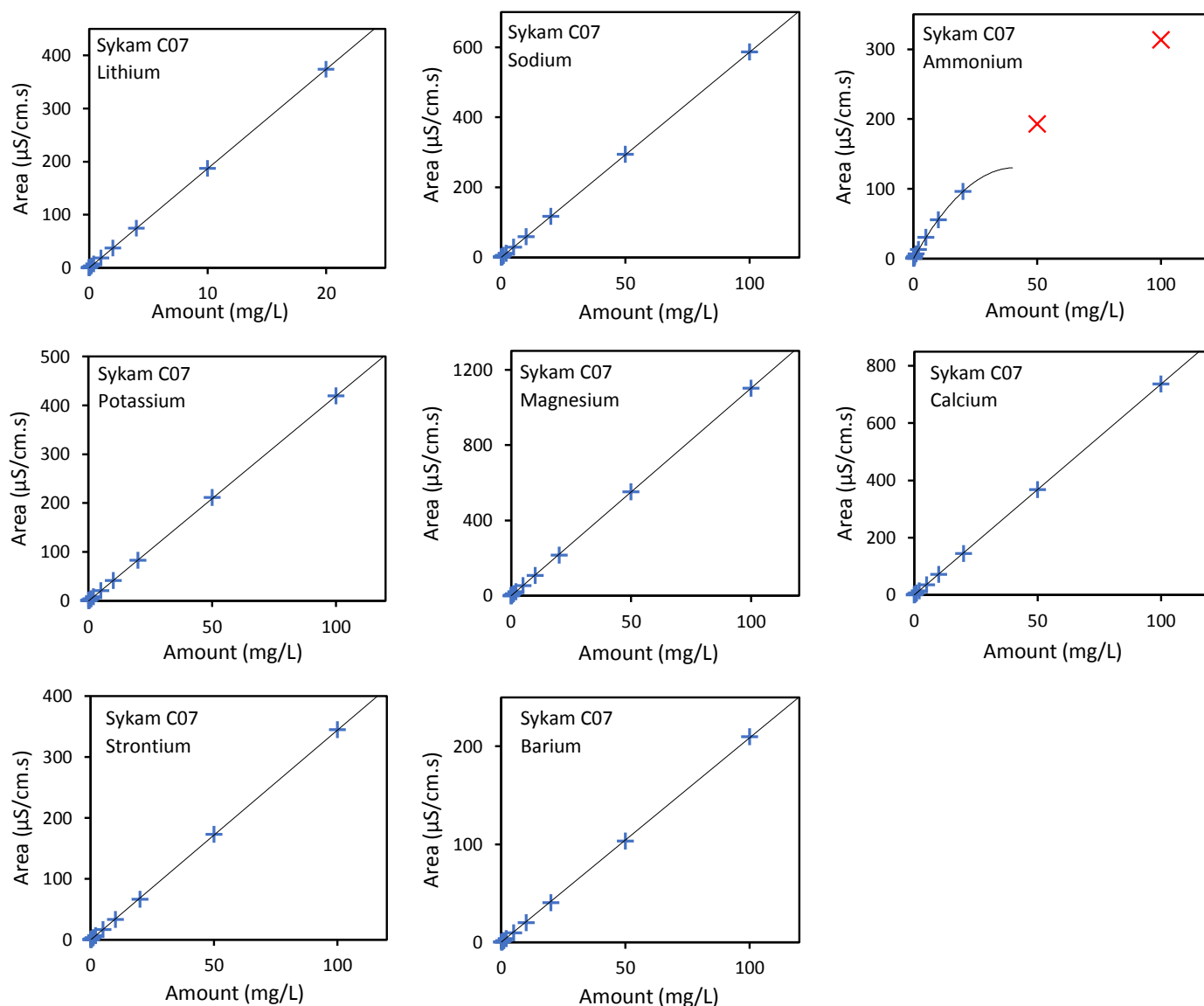


Figure 4. Calibration plots of the standard cations showing the LCR used for analysis of the samples using the Sykam C07.

### 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 ions in the QCS are similar to those found in the field samples and are listed in table 3. Tables 6 and 7 list the results of the Relative Standard Deviations (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 1.0% for all investigated ions.

If no new calibration is performed prior to analysis, the calibration standards and acceptable instrument performance are verified by the preparation and analysis of a QCS. In this case, a new calibration was performed and instrument performance was verified by analysis of an External Calibration Standard (ECS). The ECS is prepared from 1000 mg/L single ion standard stock solutions, which are prepared from a different source than the standard stock solutions used for the calibration. The QCS, however is prepared from the same standard

stock solutions that are used for the preparation of the calibration standards.

Table 5. Relative Percent Differences (RPD) of QCS and ECS.

Analyte	RPD (%) Sykam C06	RPD (%) Sykam C07
Lithium	2.0	-0.8
Sodium	0.2	-2.9
Ammonium	0.0	-2.1
Potassium	-2.7	-4.6
Magnesium	7.3	4.9
Calcium	2.6	-2.1
Strontium	-3.2	-1.0
Barium	1.7	-1.5

In table 5 the Relative Percent Differences (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 allowed deviation range of  $\pm 10\%$ .

Table 6. Linearity, MDLs, retention time and peak area precision for the Sykam C06.

Analyte	Calibration Range (mg/L)	Linearity (r <sup>2</sup> )	Calculated MDLs (µg/L)	Retention Time Precision (RSD, %)	Peak Area Precision (RSD, %)
Lithium	0.01–20	1.0000	0.1	0.25	0.53
Sodium	0.05–100	1.0000	0.2	0.25	0.50
Ammonium	0.05–20	0.9998	0.7	0.22	0.37
Potassium	0.05–100	1.0000	0.9	0.32	0.46
Magnesium	0.05–100	1.0000	1.1	0.20	0.47
Calcium	0.05–100	1.0000	3.5	0.14	0.50
Strontium	0.1–100	1.0000	26.3	0.30	0.38
Barium	0.5–100	1.0000	44.5	0.57	0.36

Table 7. Linearity, MDLs, retention time and peak area precision for the Sykam C07.

Analyte	Calibration Range (mg/L)	Linearity (r <sup>2</sup> )	Calculated MDLs (µg/L)	Retention Time Precision (RSD, %)	Peak Area Precision (RSD, %)
Lithium	0.01–20	1.0000	0.2	0.25	0.30
Sodium	0.05–100	1.0000	0.8*	0.19	0.30
Ammonium	0.05–20	0.9999	4.1	0.16	0.23
Potassium	0.05–100	1.0000	0.4*	0.11	0.24
Magnesium	0.05–100	1.0000	2.1	0.14	0.28
Calcium	0.05–100	1.0000	3.2	0.11	0.30
Strontium	0.05–100	1.0000	8.1	0.08	0.32
Barium	0.1–100	1.0000	18.6	0.07	0.31

\*Value not valid, MDL<sub>s</sub> is applied instead.

### Sample Analysis

For the validation of the Sykam C06 all six samples were analyzed undiluted after filtration. Once as initial sample and as laboratory duplicate. Since the amounts of sodium found in the drinking water sample from Karlsfeld and calcium in the stream water sample from Pitzling were not covered by the respective calibration ranges, analysis of these samples was repeated after dilution of the sample in a 1:1 ratio with deionized water. As the Sykam C07 was calibrated over the same ranges, the two samples, which were already known to exceed these ranges, were diluted for analysis, using the same dilution factors as for the C06.

Table 9 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.

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

Analyte	MRL (mg/L) Sykam C06	MRL (mg/L) Sykam C07
Lithium	0.01	0.01
Sodium	0.05	0.05
Ammonium	0.05	0.05
Potassium	0.05	0.05
Magnesium	0.05	0.05
Calcium	0.05	0.05
Strontium	0.1	0.05
Barium	0.5	0.1

Ammonium and barium were not detected in any of the drinking and natural water samples. Lithium and strontium were only detected 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 8 gives an overview of the MRLs for each cation based on the applied linear calibration range and the calculated MDLs. In the samples, potassium was found only in low concentrations between 0.65–8.3 mg/L. Sodium was found in relatively low amounts of 5.0–18.9 mg/L in all samples except for the drinking water from Karlsfeld, which contained a much higher amount of 106.9–107.0 mg/L of sodium. The detected concentrations of magnesium range from 5.9–36.4 mg/L. The amounts of calcium in the drinking and natural waters vary over a wide range of 9.4–107.2 mg/L. The results found for each sample are within a similar range for both columns.

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 both methods are suitable for the analysis of drinking and natural water samples and the reproducibility of the generated results is very high.

Table 10 summarizes the results for the two drinking water samples and the two mineral water samples. The values are compared to the supplier's analysis results. For the drinking water samples the analysis results could be found online, while the results for the mineral waters were printed on the bottle label of each mineral water. Both of the two drinking water samples and mineral water 2 correspond well with the values reported by the suppliers. The deviations are not more than 18% and less than 10% in most cases. For mineral water 1 the results found during this validation were slightly higher than reported by the supplier with deviations mostly in the range of 5–20%, except for sodium, which deviates by 41.4%. This might be due to fluctuation of the ion concentrations since the last analysis reported by the supplier.



Table 9. Analysis results (mg/L) and RPD (%) of duplicate analyses of both validations.

Analyte	Drinking Water Karlsfeld		Drinking Water Wörthsee		Mineral Water 1	
	Sykam C06	Sykam C07	Sykam C06	Sykam C07	Sykam C06	Sykam C07
Lithium	0.012 (8.7)	0.011 (0.0)	<MRL	<MRL	<MRL	<MRL
Sodium	107.0 (-0.2)	106.9 (0.2)	9.1 (0.2)	9.2 (-0.2)	13.4 (-0.1)	13.4 (0.3)
Ammonium	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Potassium	0.73 (3.6)	0.65 (3.5)	1.0 (1.1)	0.84 (0.7)	2.2 (0.9)	1.9 (1.1)
Magnesium	5.9 (0.0)	5.9 (0.3)	22.4 (0.0)	21.9 (-0.1)	36.4 (-0.2)	35.4 (0.1)
Calcium	9.5 (-0.5)	9.4 (-0.1)	87.0 (0.0)	85.4 (-0.2)	93.2 (-0.2)	90.9 (0.0)
Strontium	0.18 (3.9)	0.20 (1.0)	n.d.	0.12 (-5.0)	0.95 (-3.9)	0.68 (-4.6)
Barium	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Analyte	Mineral Water 2		Stream Water Pitzling		Lake Water Graben	
	Sykam C06	Sykam C07	Sykam C06	Sykam C07	Sykam C06	Sykam C07
Lithium	<MRL	<MRL	<MRL	<MRL	<MRL	<MRL
Sodium	13.0 (-0.3)	13.1 (-0.8)	5.0 (-0.2)	5.2 (0.0)	18.3 (0.4)	18.9 (0.1)
Ammonium	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Potassium	6.5 (-0.2)	5.9 (-0.4)	1.6 (2.8)	1.3 (2.7)	8.3 (-0.1)	7.5 (0.3)
Magnesium	9.2 (-0.3)	9.2 (-0.6)	31.6 (-0.5)	31.5 (-0.4)	23.5 (-0.5)	23.0 (0.1)
Calcium	13.0 (-0.2)	13.1 (-0.3)	107.2 (-0.5)	106.5 (-0.5)	83.9 (-0.5)	81.8 (0.1)
Strontium	n.d.	<MRL	n.d.	<MRL	n.d.	<MRL
Barium	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.

Table 10. Analysis results during method validation (mg/L) and reported analysis results (mg/L) from suppliers of drinking and mineral waters.

Analyte	Drinking Water Karlsfeld			Drinking Water Wörthsee			Mineral Water 1			Mineral Water 2		
	Sykam C06	Sykam C07	Supplier	Sykam C06	Sykam C07	Supplier	Sykam C06	Sykam C07	Supplier	Sykam C06	Sykam C07	Supplier
Sodium	107.0	106.9	110	9.1	9.2	9.5	13.4	13.4	8.8	13.0	13.1	12
Potassium	0.73	0.69	0.69	1.0	0.84	1.0	2.2	1.9	1.8	6.5	5.9	6
Magnesium	5.9	5.9	5.4	22.4	21.9	22.5	36.4	35.4	30.5	9.2	9.2	8
Calcium	9.5	9.4	9.4	87.0	85.4	86.5	93.2	90.9	79.9	13.0	13.1	12

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 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 C06, the check standards did not differ by more than 3.1% from the corresponding cation calibration standard, while the largest deviation from the corresponding calibration standard was 2.2% during the validation with the Sykam C07.

#### 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 12 and 13 list the recovery results for single-operator data for the 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 concentration of an ion after fortification would rise 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 fortified to the samples (Laboratory Fortified Blank, LFB). Table 11 summarizes the recoveries found in the Laboratory Fortified Blank for both validations.

Table 11. Recovery Data of the Laboratory Fortified Blank (LFB).

Analyte	Sykam C06		Sykam C07	
	Amount added (mg/L)	Recovery (%)	Amount added (mg/L)	Recovery (%)
Lithium	0.05	100.0	0.05	94.0
Sodium	20	102.9	20	99.9
Ammonium	1	102.7	1	96.1
Potassium	10	102.6	10	89.8
Magnesium	40	103.7	40	95.9
Calcium	15	105.6	15	99.9
Strontium	10	101.6	10	99.5
Barium	10	96.0	10	95.1

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  
 Peaks:

1. Lithium	<MRL
2. Sodium	9.1 mg/L
3. Potassium	1.0
4. Magnesium	22.4
5. Calcium	87.0

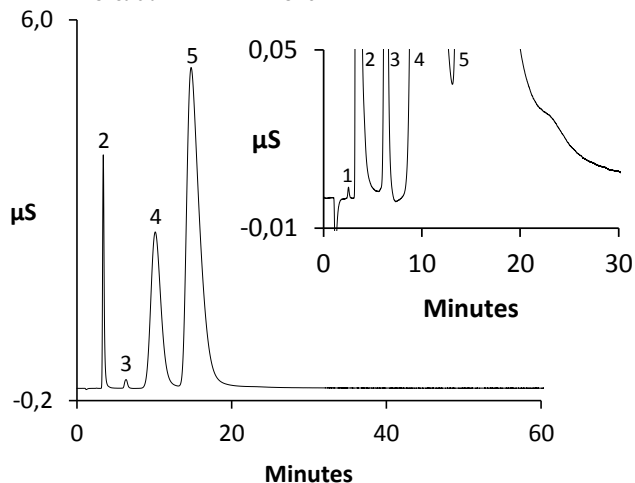


Figure 5. Determination of cations in drinking water (Wörthsee) using the Sykam C06.

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  
 Peaks:

1. Lithium	<MRL
2. Sodium	13.0 mg/L
3. Potassium	6.5
4. Magnesium	9.2
5. Calcium	13.0

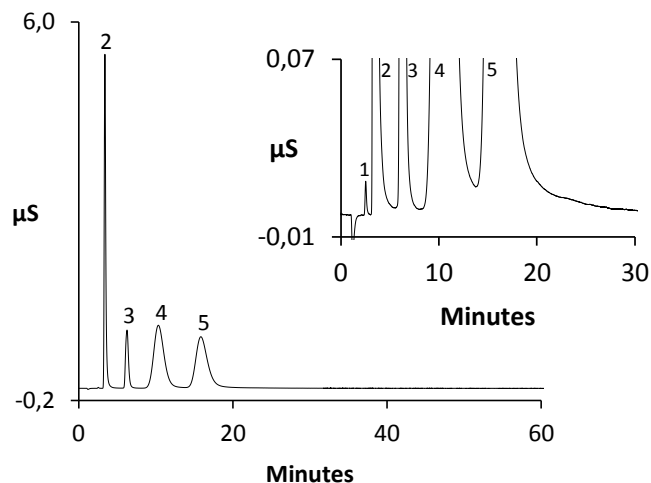


Figure 6. Determination of cations in mineral water 2 using the Sykam C06.

The recoveries in the LFB range from 96–106% for the Sykam C06 and 89–100% for the Sykam C07 respectively. Using the Sykam C06 mostly good recoveries of the cations of 84–108% were obtained for the fortified samples. The recovery of barium was low in mineral water sample 1 (46%). This sample was analyzed a few hours after it was prepared. In the sample a colorless precipitate was formed. According to the supplier, mineral water 1 contains 113.7 mg/L of sulfate, which

forms the barely water-soluble barium sulfate ( $\text{BaSO}_4$ ) with barium. In another sample of the LFM of mineral water 1 that was analyzed immediately after it was prepared the recovery of barium was 84.9%. Therefore, samples containing high amounts of sulfate should be analyzed immediately when spiked with barium. With the Sykam C07 good recoveries between 84–104% were found.

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: Suppressed Conductivity  
 Peaks:

1. Lithium	<MRL
2. Sodium	13.4 mg/L
3. Potassium	1.9
4. Magnesium	35.4
5. Calcium	90.9
6. Strontium	0.68

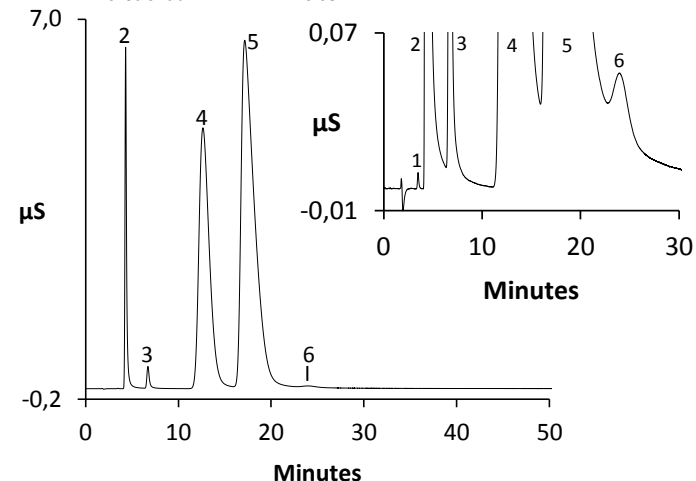


Figure 7. Determination of cations in mineral water 1 using the Sykam C07.

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: Suppressed Conductivity  
 Peaks:

1. Lithium	<MRL
2. Sodium	18.9 mg/L
3. Potassium	7.5
4. Magnesium	23.0
5. Calcium	81.8
6. Strontium	<MRL

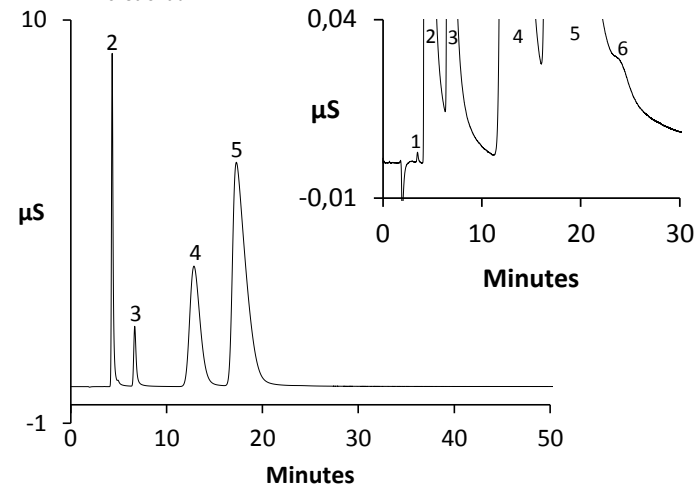


Figure 8. Determination of cations in lake water using the Sykam C07.

Table 12. Recovery Data from fortified Drinking and Natural Water Samples using the Sykam C06.

Analyte	Drinking Water Karlsfeld		Drinking Water Wörthsee		Mineral Water 1 (Diluted 1:1)	
	Amount added (mg/L)	Recovery (%)	Amount added (mg/L)	Recovery (%)	Amount added (mg/L)	Recovery (%)
Lithium	0.05	97.9	0.05	98.2	0.05	100.6
Sodium	–	–	10	103.4	15	102.4
Ammonium	1	100.0	1	100.3	1	100.6
Potassium	0.5	103.0	2	101.7	5	101.7
Magnesium	5	105.7	25	106.7	40	101.1
Calcium	5	106.5	–	–	–	–
Strontium	10	101.3	10	106.3	10	99.8
Barium	10	96.0	10	98.0	10	46.3
Analyte	Mineral Water 2		Stream Water Pitzling		Lake Water Graben	
	Amount added (mg/L)	Recovery (%)	Amount added (mg/L)	Recovery (%)	Amount added (mg/L)	Recovery (%)
Lithium	0.05	103.1	0.05	96.0	0.05	98.2
Sodium	15	102.3	5	102.2	20	101.6
Ammonium	1	106.8	1	94.2	1	99.0
Potassium	10	103.4	1	107.6	10	102.0
Magnesium	10	104.9	20	105.3	25	103.6
Calcium	15	103.3	–	–	–	–
Strontium	10	101.1	10	101.0	10	104.0
Barium	10	95.2	10	97.0	10	95.3

Table 13. Recovery Data from fortified Drinking and Natural Water Samples using the Sykam C07.

Analyte	Drinking Water Karlsfeld (Diluted 1:1)		Drinking Water Wörthsee		Mineral Water 1	
	Amount added (mg/L)	Recovery (%)	Amount added (mg/L)	Recovery (%)	Amount added (mg/L)	Recovery (%)
Lithium	0.05	97.3	0.05	94.2	0.05	92.6
Sodium	–	–	10	97.4	15	96.0
Ammonium	1	96.6	1	92.9	1	91.1
Potassium	0.5	98.2	2	96.6	5	91.5
Magnesium	5	96.2	25	97.0	40	94.7
Calcium	5	96.5	–	–	–	–
Strontium	10	98.1	10	99.8	10	95.4
Barium	10	98.7	10	93.8	10	92.2
Analyte	Mineral Water 2		Stream Water Pitzling (Diluted 1:1)		Lake Water Graben	
	Amount added (mg/L)	Recovery (%)	Amount added (mg/L)	Recovery (%)	Amount added (mg/L)	Recovery (%)
Lithium	0.05	90.2	0.05	92.0	0.05	84.2
Sodium	15	93.7	5	95.3	20	85.5
Ammonium	1	91.3	1	93.9	1	96.4
Potassium	10	89.5	1	96.7	10	84.5
Magnesium	10	92.4	20	93.3	25	86.2
Calcium	15	92.5	–	–	–	–
Strontium	10	98.5	10	104.0	10	100.3
Barium	10	90.0	10	91.8	10	84.8

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

Peaks:	1. Lithium	<MRL	0.10 mg/L
	2. Sodium	5.0	15.0
	3. Ammonium	-	1.9
	4. Potassium	1.6	3.7
	5. Magnesium	31.6	72.2
	6. Calcium	107.2	103.4
	7. Strontium	-	20.2
	8. Barium	-	19.4

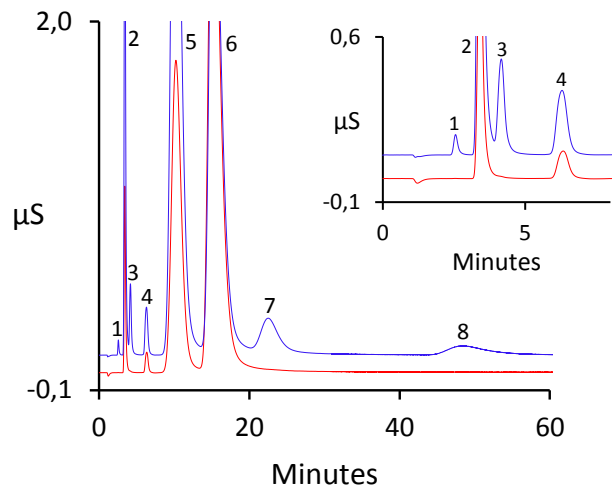


Figure 8. Determination of cations in spiked (blue) and unspiked (red) diluted (1:1) stream water samples using the Sykam C06.

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: Suppressed Conductivity

Peaks:	1. Lithium	0.011	0.11 mg/L
	2. Sodium	106.7	108.0
	3. Ammonium	-	1.9
	4. Potassium	0.65	1.6
	5. Magnesium	5.9	15.3
	6. Calcium	9.4	18.8
	7. Strontium	0.19	19.8
	8. Barium	-	19.7

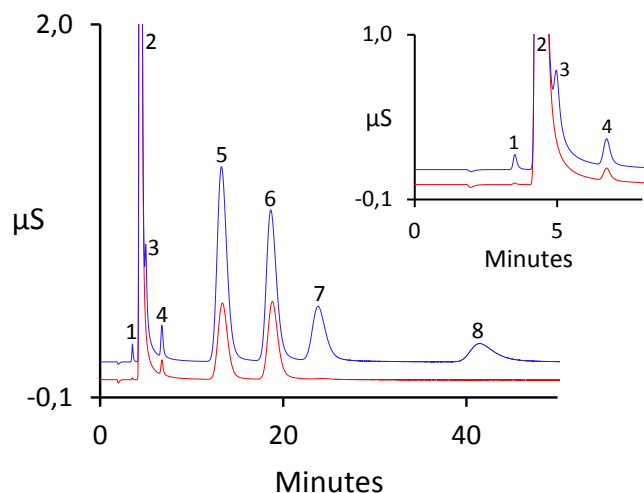


Figure 10. Determination of cations in spiked (blue) and unspiked (red) diluted (1:1) drinking water samples (Karlsfeld) using the Sykam C07.

## Summary

The Sykam C06 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 C06, as well as the Sykam C07 have a high resolution for all examined cations, making them suitable for the analyses of complex matrices or large concentration differences between closely eluting peak pairs. All cations except for lithium and ammonium can be calibrated over a wide range. For the determination of the common cations with or without strontium, the run times are similar for both columns, but for the determination of barium the run time is significantly shorter when using the Sykam C07. The run times can be shortened if strontium and barium are not determined. For analysis with focus on the alkaline earth metals, especially when determining strontium and barium, we recommend to use the Sykam C07 due to the narrower peak shapes. If the determination of ammonium is of importance, we recommend the use of the Sykam C06 as this column provides better resolution between sodium and ammonium.

## References

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- [6] [www.epa.gov/ground-water-and-drinking-water/national-primary-drinking-water-regulations](http://www.epa.gov/ground-water-and-drinking-water/national-primary-drinking-water-regulations) (accessed December 10, 2024).
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- [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<sup>+</sup>, Na<sup>+</sup>, NH<sub>4</sub><sup>+</sup>, K<sup>+</sup>, Mn<sup>2+</sup>, Ca<sup>2+</sup>, Mg<sup>2+</sup>, Sr<sup>2+</sup> and Ba<sup>2+</sup> 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).

[www.sykam.com](http://www.sykam.com)

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