Application Work AW IC CH-1556-032026

Fast determination of standard anions in drinking water according to DIN EN ISO 10304-1 with the Metrosep A Supp 19 - 50/4.0 column

Industry sector

S02 Environmental testing; S021 Drinking water

Keywords

IC; anions; water; standard anions; fluoride; F^-; chloride; Cl^-; nitrite; NO_2^-; bromide; Br^-; nitrate; NO_3^-; sulfate; SO_4^{2-}; phosphate; PO_4^{3-}; tap water; drinking water; bottled water; Metrosep A Supp 19 - 50/4.0; 930 Compact IC; 858 Professional Sample Processor; MSM A; MagIC Net 4.2; carbonate eluent; chemical suppression; STREAM; conductivity; ISO 10304-1; fast determination; environmental testing; S02; S021

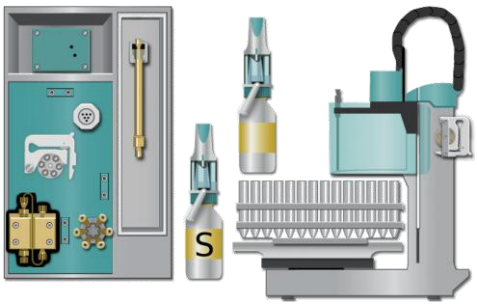
Summary

This application work describes a method for the determination of the standard anions using the Metrosep A Supp 19 - 50/4.0 according to the DIN EN ISO 10304-1 standard in less than 5 minutes. Elution is done with an isocratic carbonate/bicarbonate eluent at 30°C. Injection is done using direct injection with a 10 µL loop. With this technique, close to 300 samples can be determined per day!

Samples

Metrohm tap water; Herisau tap water; Evian bottled water (still water; Eau Minerale Naturelle; Quelle Cachat; declared mineral concentrations 80 mg/L Ca^{2+}; 26 mg/L Mg^{2+}; 6.5 mg/L Na^+; 1 mg/L K^+; 15 mg/L SiO_2; 360 mg/L HCO_3^-; 14 mg/L SO_4^{2-}; 10 mg/L Cl^-; 3.8 mg/L NO_3^-).

Instruments and accessories



Article no.	
2.930.2560	930 Compact IC Flex Oven/SeS/PP/Deg
2.850.9020	IC Conductivity Detector MB
2.858.0010	858 Professional Sample Processor
6.2832.000	MSM Rotor A
2.800.0010	800 Dosino
6.3032.120	Dosing unit 2 mL
6.01034.450	Metrosep A Supp 19 - 50/4.0
6.01034.500	Metrosep A Supp 19 Guard/4.0
6.6059.421	MagIC Net 4.2 Compact

Reagents

- Anion standards for IC, TraceCERT®, from Sigma Aldrich
  - Fluoride, β(F^-) = 1 g/L in H_2O; No. 77365
  - Chloride, β(Cl^-) = 1 g/L in H_2O; No. 39883
  - Nitrite, β(NO_2^-) = 1 g/L in H_2O; No. 67276
  - Bromide, β(Br^-) = 1 g/L in H_2O; No. 43147
  - Nitrate, β(NO_3^-) = 1 g/L in H_2O; No. 74246
  - Sulfate, β(SO_4^{2-}) = 1 g/L in H_2O; No. 90071
  - Phosphate. β(PO_4^{3-}) = 1 g/L in H_2O; No. 38364
- Ultrapure water, resistivity >18 MΩ·cm (25 °C), type I grade (ASTM D1193)
- Sodium carbonate, Na_2CO_3, anhydrous, for analysis EMSURE® ACS, ISO, Reag. Ph. Eur., CAS 497-19-8, Sigma-Aldrich, Merck 1.06393

- Sodium bicarbonate, $NaHCO_3$, purris. p.a., ACS reagent, Read. Ph. Eur., ≥ 99.7%, CAS 144-55-8, Sigma-Aldrich, Merck 31437
- Sulfuric acid, H_2SO_4, 95-97%, CAS 7664-38-2, Sigma Aldrich 30743

Solutions

Eluent	$c(Na_2CO_3)$ = 8.0 mmol/L $c(NaHCO_3)$ = 0.25 mmol/L
Suppressor reg.	$c(H_2SO_4)$ = 200 mmol/L

Standard solutions

In ultrapure water, µg/L:

Analyte	Abbreviation	Standard 1 mg/L
Fluoride	F^-	10
Chloride	Cl^-	50
Nitrite	NO_2^-	50
Bromide	Br^-	50
Nitrate	NO_3^-	100
Phosphate	PO_4^{3-}	100
Sulfate	SO_4^{2-}	100

Sample preparation

Samples were injected without any prior sample preparation. Standards 2 - 7 were prepared by manual dilution of from standard 1 (Dilution factors: 2, 5, 10, 20, 50, 100).

Analysis

Samples and standards were injected directly with a fixed loop size of 10 µL.

Parameters for IC

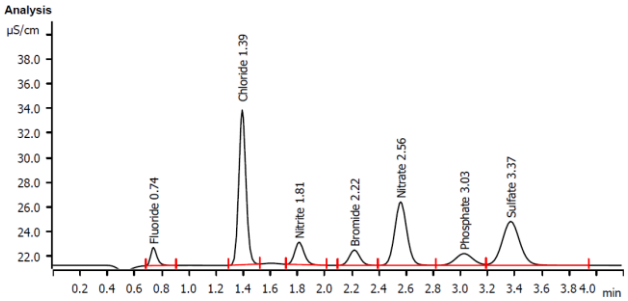
Flow rate eluent	1.2 mL/min
Start-up time	2 min
Maximum pressure	20 MPa
Column temperature	30 °C
Recording time	4.2 min
Sample volume	10 µL
Suppression	Chemical suppression
MSM stepping interval	4 min
Dosino regeneration volume	2.0 mL
Detector polarity	+
Detector temperature coefficient	2.3 %/°C

Calculations

Calculation was performed by automatic integration with the MagIC Net 4.2 software using peak area for all analytes and manual correction where necessary.

Example chromatogram

Herisau tap water sample, spiked with 1 mg/L fluoride, 5 mg/L chloride, nitrite, and bromide, 10 mg/L nitrate, sulfate, and phosphate.



Results

All results are the mean value of 3 determinations.

Metrohm Tap water

Analyte	Metrohm tap		Metrohm tap spiked(*)		
	µg/L	RSD	µg/L	RSD	Rec
F^-	48	7.4%	945	1.7%	90.1%
Cl^-	9'209	2.1%	13'333	0.6%	99.1%
NO_2^-	157	4.5	4'853	4.0%	94.2%
Br^-	35	11.0%	4'834	1.7%	96.1%
NO_3^-	8'780	1.9%	17'689	0.9%	97.0%
PO_4^{3-}	n.d.	-	9.558	1.4%	95.6%
SO_4^{2-}	4'503	1.3%	13'624	1.0%	95.3%

Application Work AW IC CH-1556-032026
Fast determination of standard anions in drinking water according to DIN EN ISO 10304-1 with the Metrosep A Supp 19 - 50/4.0 column

Herisau Tap water

Analyte	Herisau tap		Herisau tap spiked(*)		
	µg/L	RSD	µg/L	RSD	Rec
F^-	55	11.3%	962	2.0%	91.2%
Cl^-	8'883	0.8%	12'776	0.4%	93.8%
NO_2^-	175	10.4%	4'893	3.9%	94.7%
Br^-	65	23.3%	4'869	1.6%	96.2%
NO_3^-	8'627	1.8%	17'274	0.8%	94.2%
PO_4^{3-}	n.d.	-	9'627	1.4%	96.3%
SO_4^{2-}	5'252	2.7%	14'226	0.9%	94.5%

Evian mineral water

Analyte	Evian		Evian spiked(*)		
	µg/L	RSD	µg/L	RSD	Rec
F^-	76	25.7%	948	2.0%	87.9%
Cl^-	11'168	0.4%	14'881	0.5%	94.4%
NO_2^-	176	11.2%	4'862	3.9%	94.0%
Br^-	60	22.4%	4'820	1.8%	95.3%
NO_3^-	4'307	6.7%	13'087	1.3%	91.7%
PO_4^{3-}	n.d.	-	9'549	1.7%	95.5%
SO_4^{2-}	13'824	0.2%	22'205	0.7%	96.3%

Artificial Tap water (300 mg/L HCO_3^- from $NaHCO_3$)

Analyte	Artificial tap (**)		Artificial tap spiked(*)		
	µg/L	RSD	µg/L	RSD	Rec
F^-	8	-	912	1.6%	90.5%
Cl^-	311	-	4'690	1.5%	88.1%
NO_2^-	169	-	4'904	3.8%	95.0%
Br^-	48	-	4'799	2.0%	95.1%
NO_3^-	293	-	9'547	1.9%	92.8%
PO_4^{3-}	97	-	9'581	1.8%	94.9%
SO_4^{2-}	336	-	9'615	1.6%	92.8%

* - spiked with 1 mg/L fluoride, 5 mg/L chloride, nitrite, bromide, 5 mg/L nitrate, phosphate, sulfate. The spiking volume was 10% of the total volume.

** - only one valid sample available

Comments

The Metrosep A Supp 19 column is a carbonate-selective column and is well known on the market for the determination of the standard anions according to DIN EN ISO 10304-1 conditions. The 50/4.0 version allows a very fast analysis in the mg/L concentration range for this norm.

The DIN EN ISO 10304-1 has a few requirements that need to be met:

- A minimum resolution of 1.3 between all ions must be obtained to guarantee accurate quantification.
- The retention times of the ions of interest cannot vary by more than 10% within one sample run.
- Spiking recoveries are not explicitly mentioned in the DIN EN ISO 10304-1 standard. For this reason, it was decided to check the recoveries against the requirements of the US EPA 300.1 A standard: Recoveries must lie between 85% and 115% for high concentrations and between 75% and 125% for lower concentrations (maximum 10 times the "minimum reporting level", which corresponds to the lower calibration standard).

As can be seen in the result tables, the recoveries meet the requirements from the norm:

- In Metrohm tap water, the spiking recoveries range between 90.1% and 99.1%, meeting the norm requirements.
- In Herisau tap water, the spiking recoveries range between 91.2% and 96.3%, meeting the norm requirements.
- In Evian mineral water, the spiking recoveries range between 87.9% and 96.3%, meeting the norm requirements.
- In the artificial carbonate sample matrix, the recoveries range between 88.1% and 95.1%, meeting the norm requirements.

To verify the method robustness, all the samples were analyzed 3 times, and the RSD was calculated. Thereby, RSDs were below 4.0% for all analytes in concentrations higher than 1 mg/L. At lower concentrations, higher RSDs were

Application Work AW IC CH-1556-032026
Fast determination of standard anions in drinking water according to DIN EN ISO 10304-1 with the Metrosep A Supp 19 - 50/4.0 column

seen, most likely because the injection technique and the carryover and rinsing procedure was not yet optimized for this method.

The DIN EN ISO 10304 Part 1 requires a minimum resolution of 1.3 for proper quantification. It was found that the resolution between phosphate and sulfate is the most critical one. Throughout the series of measurements, the resolution between phosphate and sulfate was at least at 1.38 (Average: 1.46 ± 2.4%). This is sufficient to guarantee appropriate quantification.

With the method using the Metrosep A Supp 19 - 50/4.0 shown here, a run time of 4.2 minutes is achieved, which is much faster than any other (competitor) column can provide, making this analysis very competitive. Potentially, the flow rate can be further increased up to 1.8 mL/min, leading to chromatogram durations below 3 minutes (care needs to be given to the phosphate to sulfate resolution). Corresponding chromatograms are shown in the appendix, see Figure 15.

Matrix compatibility is always a big issue when it comes to the analysis of drinking waters. The effect of several matrix components was tested regarding the separation quality. In particular, the effect of large quantities of chloride, nitrate, sulfate, and carbonate was tested. Also, the position of the early eluting organic acids acetate, and formate was tested. Thereby, the reference sample was composed of 1 mg/L fluoride, 5 mg/L chloride, nitrite, bromide, 10 mg/L nitrate, phosphate, and sulfate.

- To test the method robustness against chloride in the sample, an artificial sample containing 200 mg/L chloride was measured. As can be observed in figure 10, the chloride peak expands to the right under the chosen elution conditions. This means that the nitrite peak, which appears in the tailing of chloride (at high chloride concentrations), can get affected at high chloride concentrations. Up to chloride concentrations of 200 mg/L in the sample, recovery requirements for nitrite can be maintained.

- On the Metrosep A Supp 19, large concentrations of nitrate in the sample could have an effect on the determination of phosphate, because the nitrate peak expands mostly to the right, in a similar way to the chloride peak (see figure 11). At concentrations higher than 100 mg/L nitrate, the accurate determination of 10 mg/L phosphate is still possible.

- Depending on the water source, sulfate can also be present in large concentrations in drinking water samples. Since the sulfate peak elutes as the last peak, it can only affect the phosphate peak (see figure 12). However, for sulfate concentrations of up to 200 mg/L, no decrease in phosphate recovery was observed.

- In water samples, the presence of carbonate in the sample can cause disturbances with the determination of the other anions. Carbonate matrix compatibility was tested using the artificial tap water sample containing 300 mg/L carbonate (from sodium bicarbonate). In this method, the position of the carbonate peak is just behind chloride, but did not give any issues for the determination of the neighboring peaks (figure 13).

At higher concentrations of chloride, nitrate, sulfate, or carbonate, it is recommended to work with the longer column, the Metrosep A Supp 19 - 100/4.0 (keep in mind that this will also increase the total run time).

The early eluting organic acids formate and acetate are often found in drinking water samples and should therefore not show any coelution with the anions of interest. Thereby, the elution order is fluoride, acetate, formate, and chloride (see figure 14).

All the analyzes done in the application were done with the 940 Professional IC, but of course, this application can also be performed on the 930 Compact IC. To optimize the dead volume of the instrument, the instrument was set up as a microbore system (e.g. 2.930.2580).

In the tests performed here, the column pressure was around 9.1 MPa (at 30 °C), leaving enough space for column ageing, as the maximum pressure of the Metrosep A Supp 19 - 50/4.0 is set to 20 MPa, ensuring a high long-term stability.

References

DIN EN ISO 10304-1 standard

Date

March 2026

Author

Vincent Diederich

Competence Center Ion Chromatography

Metrohm International Headquarters

Appendix

1. Experimental Setup
2. Standards and Calibration
3. Impact of chloride on chromatogram
4. Impact of nitrate on chromatogram
5. Impact of sulfate on chromatogram
6. Impact of carbonate on chromatogram
7. Position of the early eluting organic acids
8. Even faster analysis

Appendix

1. Experimental Setup

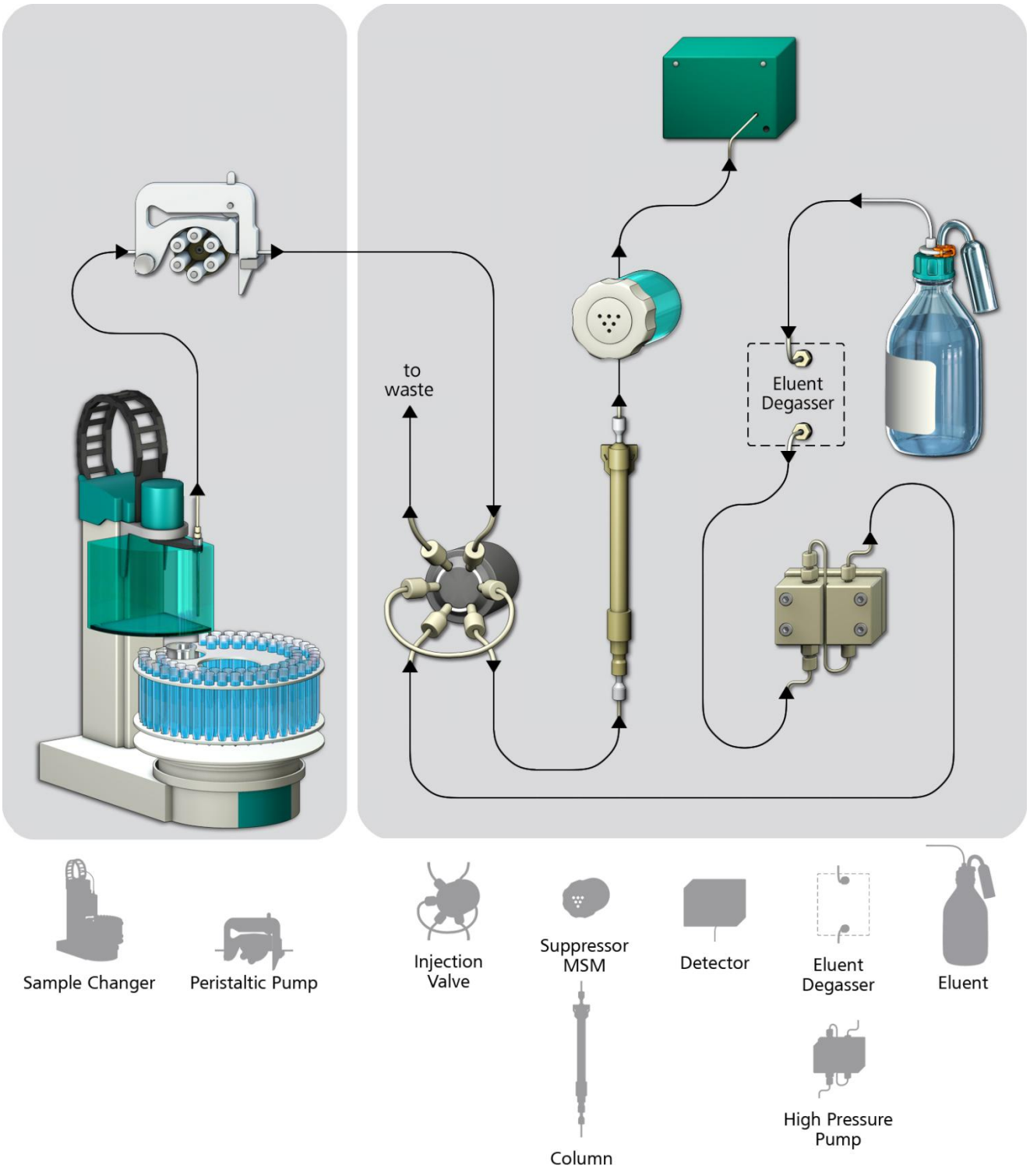


Figure 1. System setup.

Application Work AW IC CH-1556-032026
Fast determination of standard anions in drinking water according to DIN EN ISO 10304-1 with the Metrosep A Supp 19 - 50/4.0 column

2. Standards and Calibration

Overlay of the calibration standards

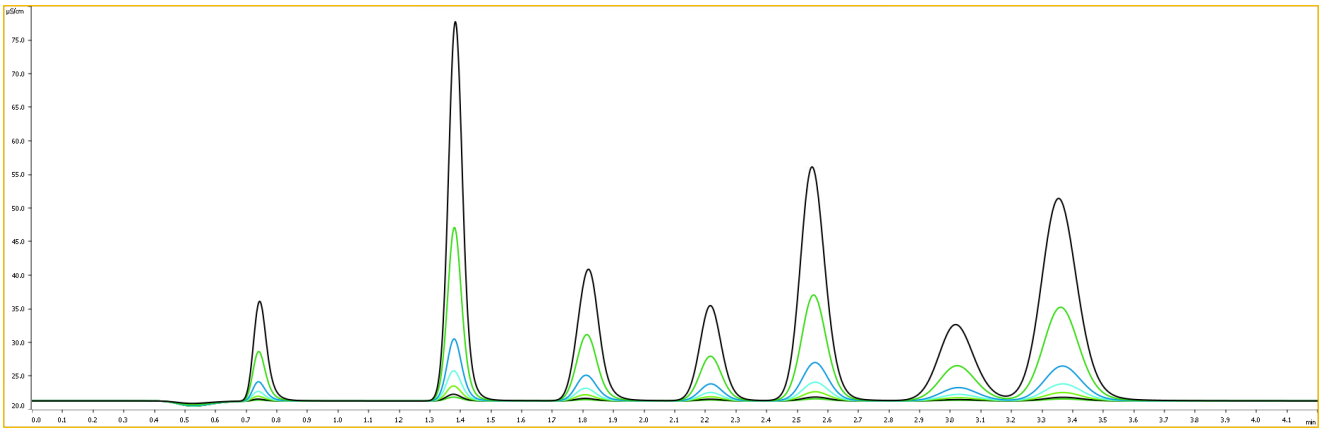


Figure 2. Overlay of standard chromatograms in ultrapure water.

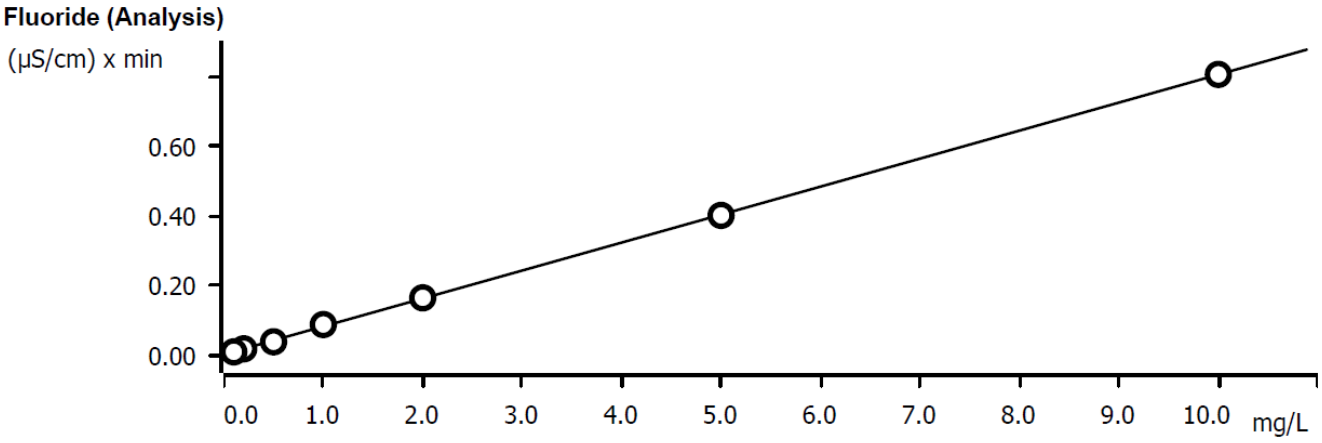


Figure 3. Fluoride quadratic calibration curve.

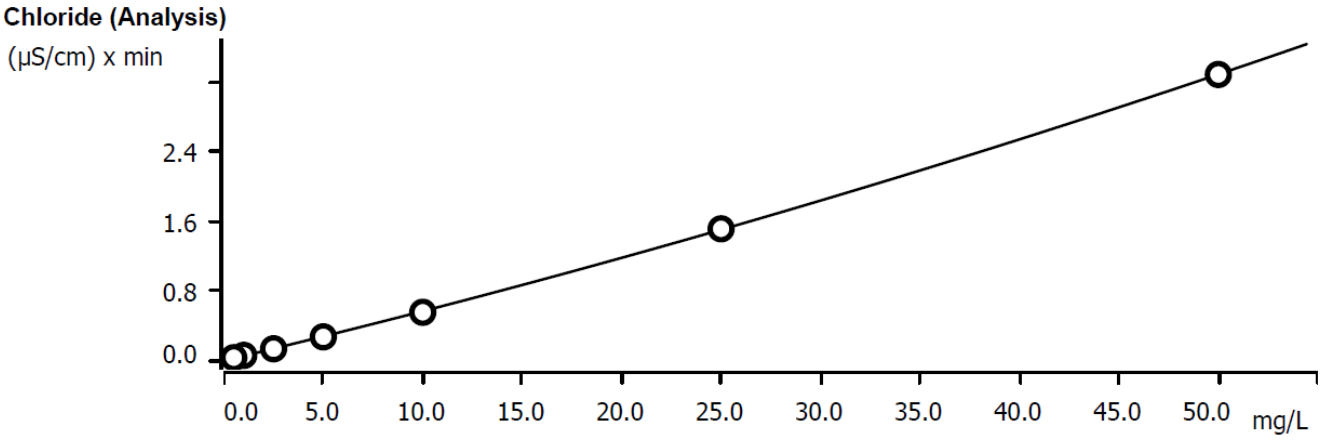


Figure 4. Chloride quadratic calibration curve.

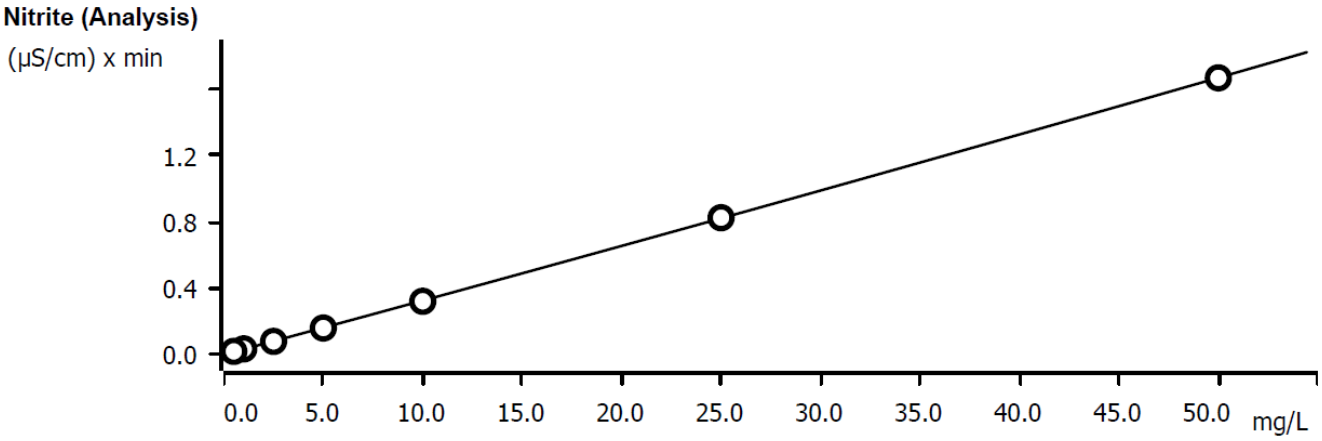


Figure 5. Nitrite quadratic calibration curve.

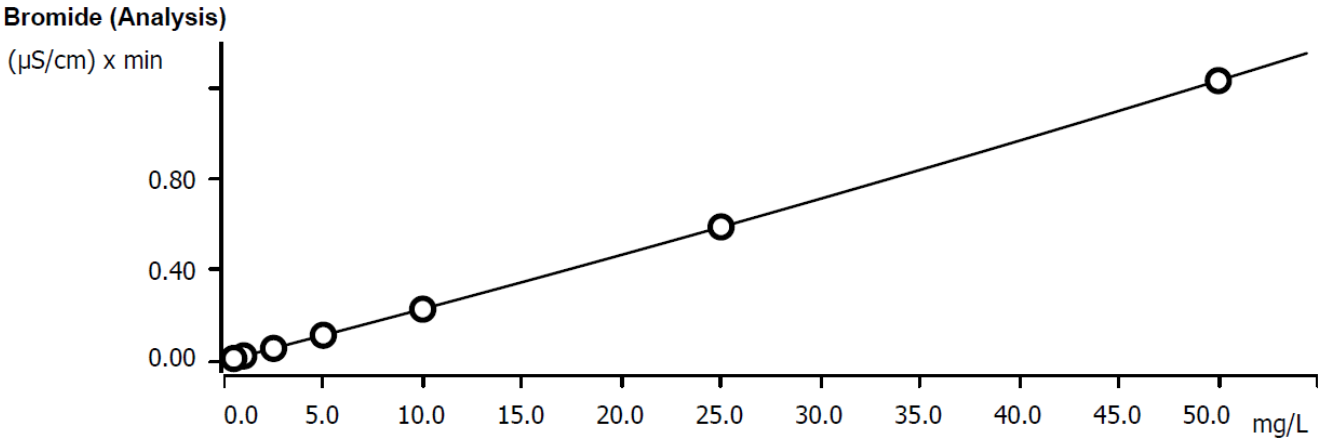


Figure 6. Bromide quadratic calibration curve.

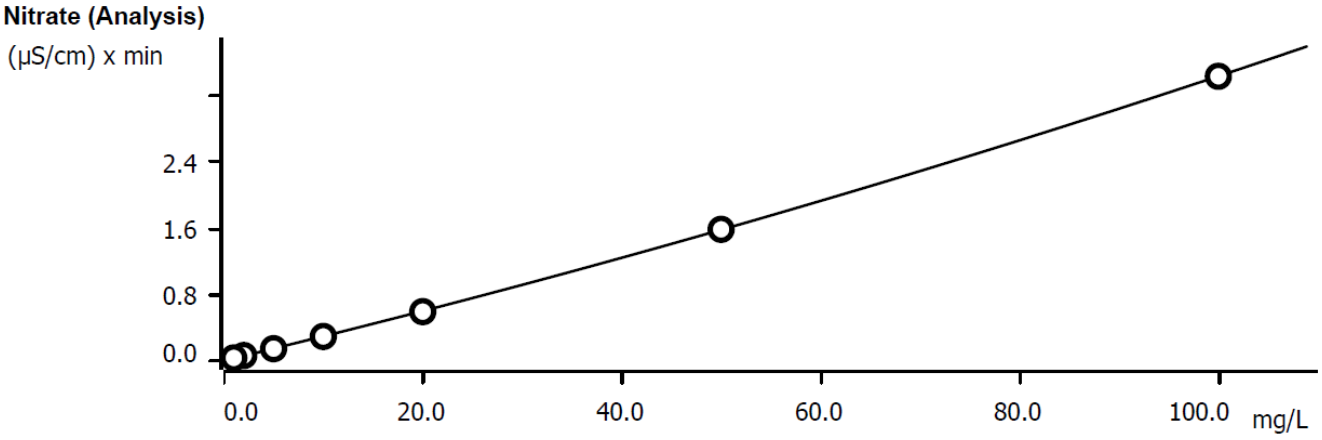


Figure 7. Nitrate quadratic calibration curve.

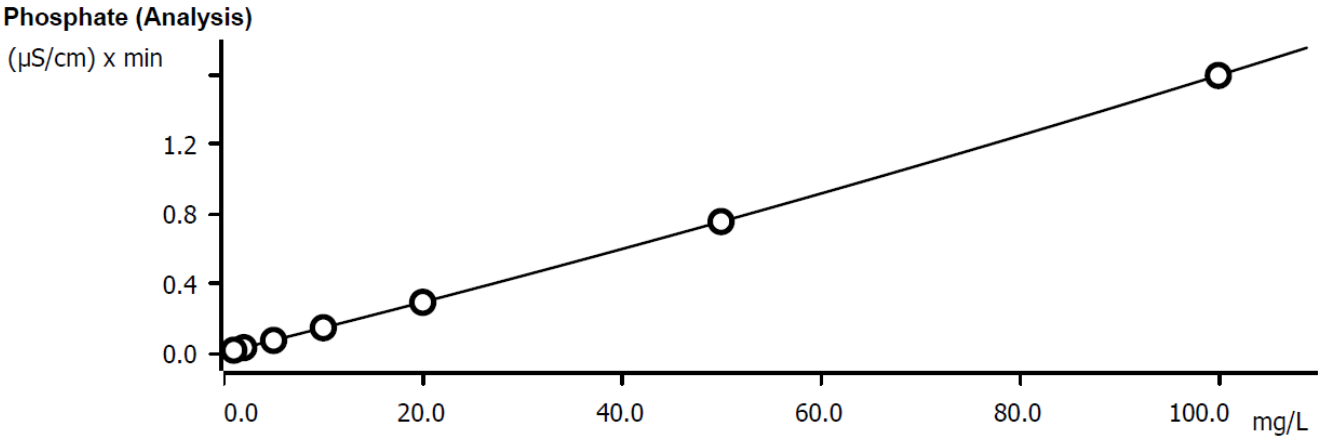


Figure 8. Phosphate quadratic calibration curve.

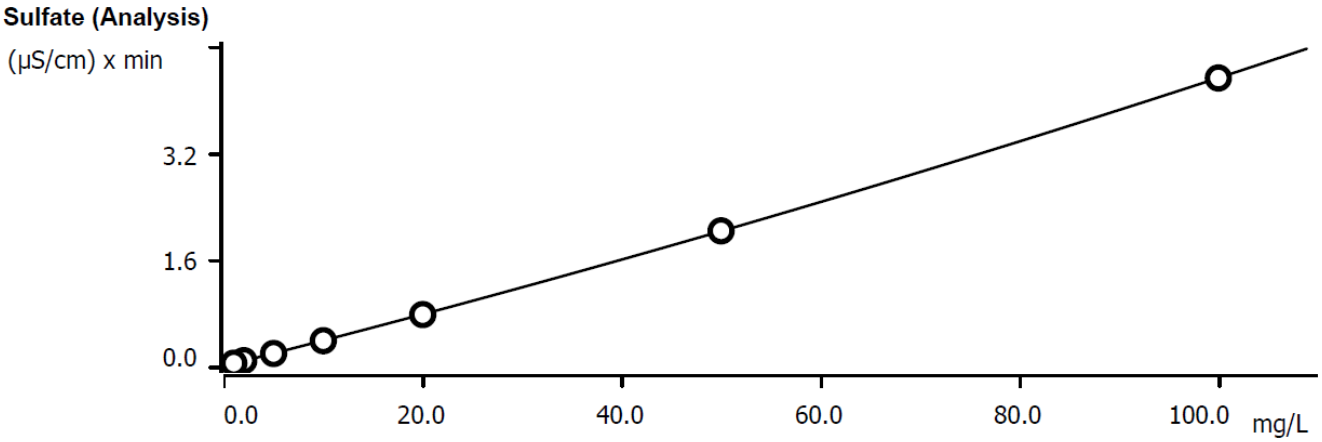


Figure 9. Sulfate quadratic calibration curve.

Analyte	Factor k(0)	Factor k(1)	Factor (k2)	RSD (%)	Correlation coefficient
Fluoride	1.66321E-3	8.01714E-3	1.89642E-7	1.72%	0.999946
Chloride	1.45527E-3	5.45644E-3	2.24622E-6	1.14%	0.999979
Nitrite	-4.40700E-3	3.24473E-3	2.07617E-7	0.81%	0.999989
Bromide	9.93992E-4	2.24376E-3	4.31947E-7	0.22%	0.999999
Nitrate	3.84646E-4	2.88868E-3	5.51338E-7	0.62%	0.999994
Phosphate	1.56831E-3	1.41794E-3	1.75109E-7	0.18%	0.999999
Sulfate	2.85242E-3	3.79690E-3	5.57907E-7	0.45%	0.999997

3. Impact of chloride on chromatogram

The overlay below shows the effect of chloride in the sample on the separation performance of the neighboring peaks, in particular nitrite (at ca. 2.2 min). Even for chloride concentrations up to 200 mg/L, 5.0 mg/L nitrite can be determined reliably.

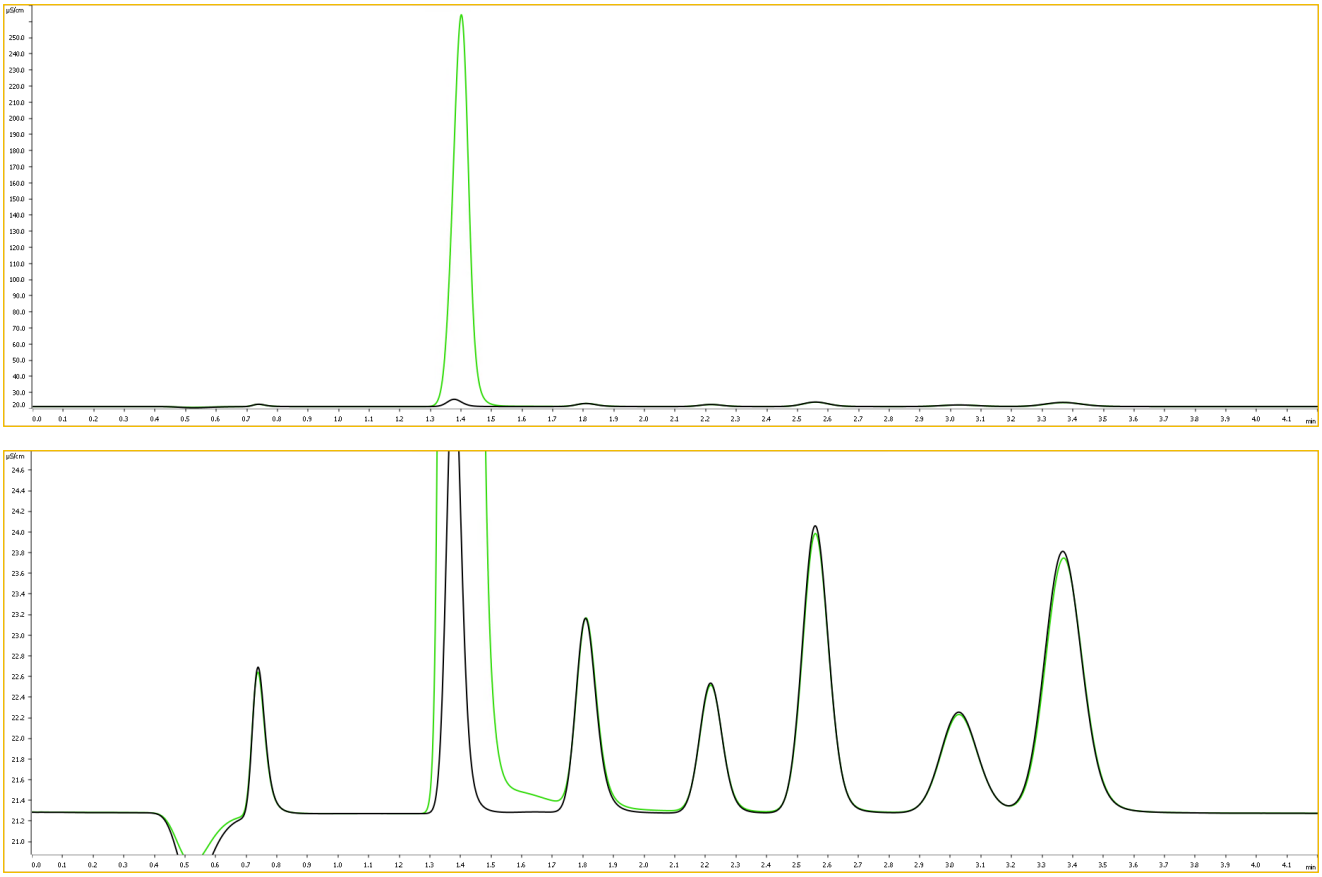
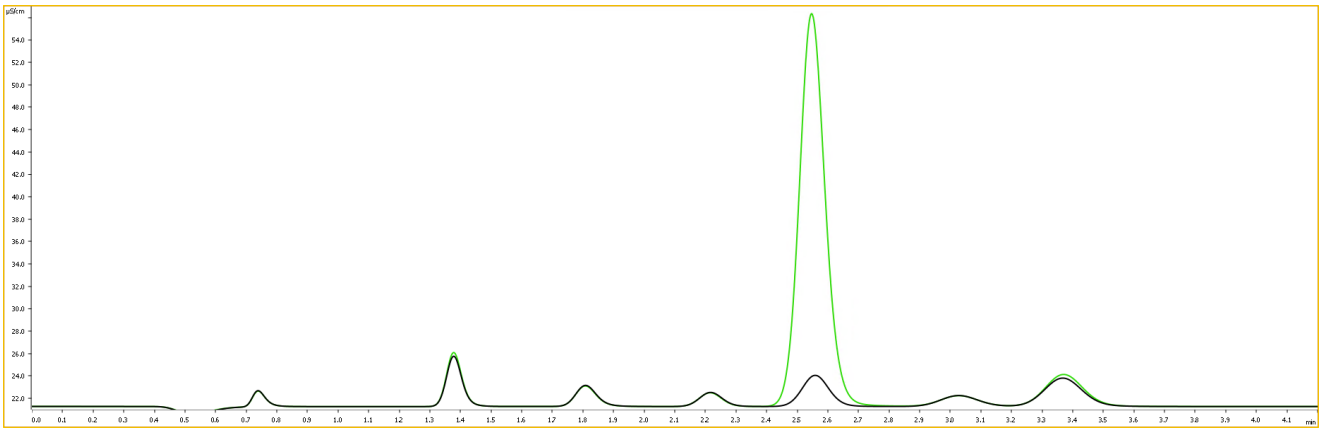


Figure 10. Overlay of artificial samples with different concentrations of chloride (black: 5 mg/L, green: 200 mg/L).

4. Impact of nitrate on chromatogram

The overlay below shows the effect of nitrate in the sample on the separation performance of the neighboring peaks, in particular phosphate (at ca. 3.0 min). Up to nitrate concentrations of 1000 mg/L, all analytes can be determined reliably, especially bromide at 5 mg/L and phosphate at 10 mg/L.



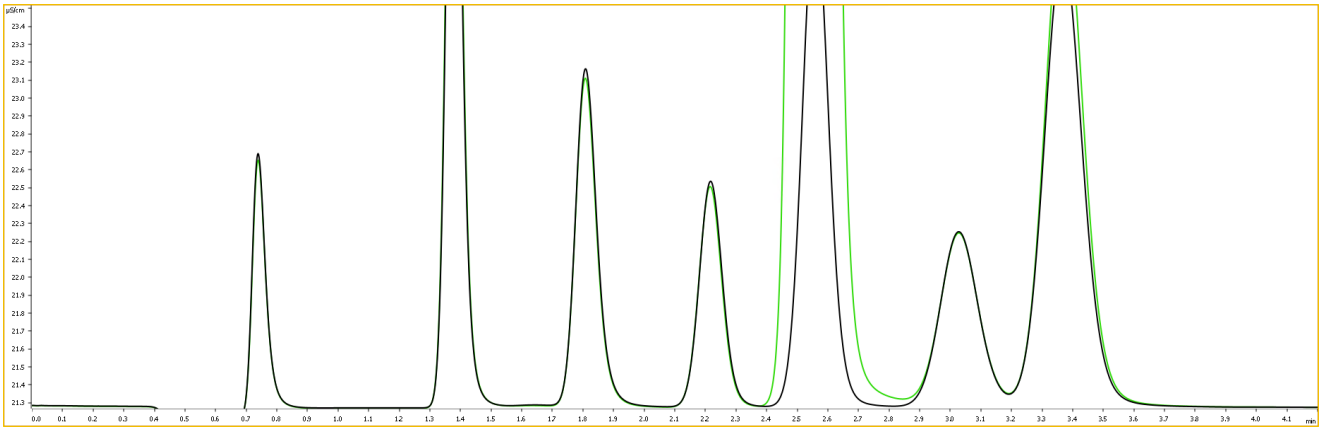


Figure 11. Overlay of artificial samples with different concentrations of nitrate (black: 10 mg/L, green: 100 mg/L).

5. Impact of sulfate on chromatogram

The overlay below shows the effect of sulfate in the sample on the separation performance. Even for sulfate concentrations up to 200 mg/L, all analytes can be determined reliably, especially phosphate at 10 mg/L.

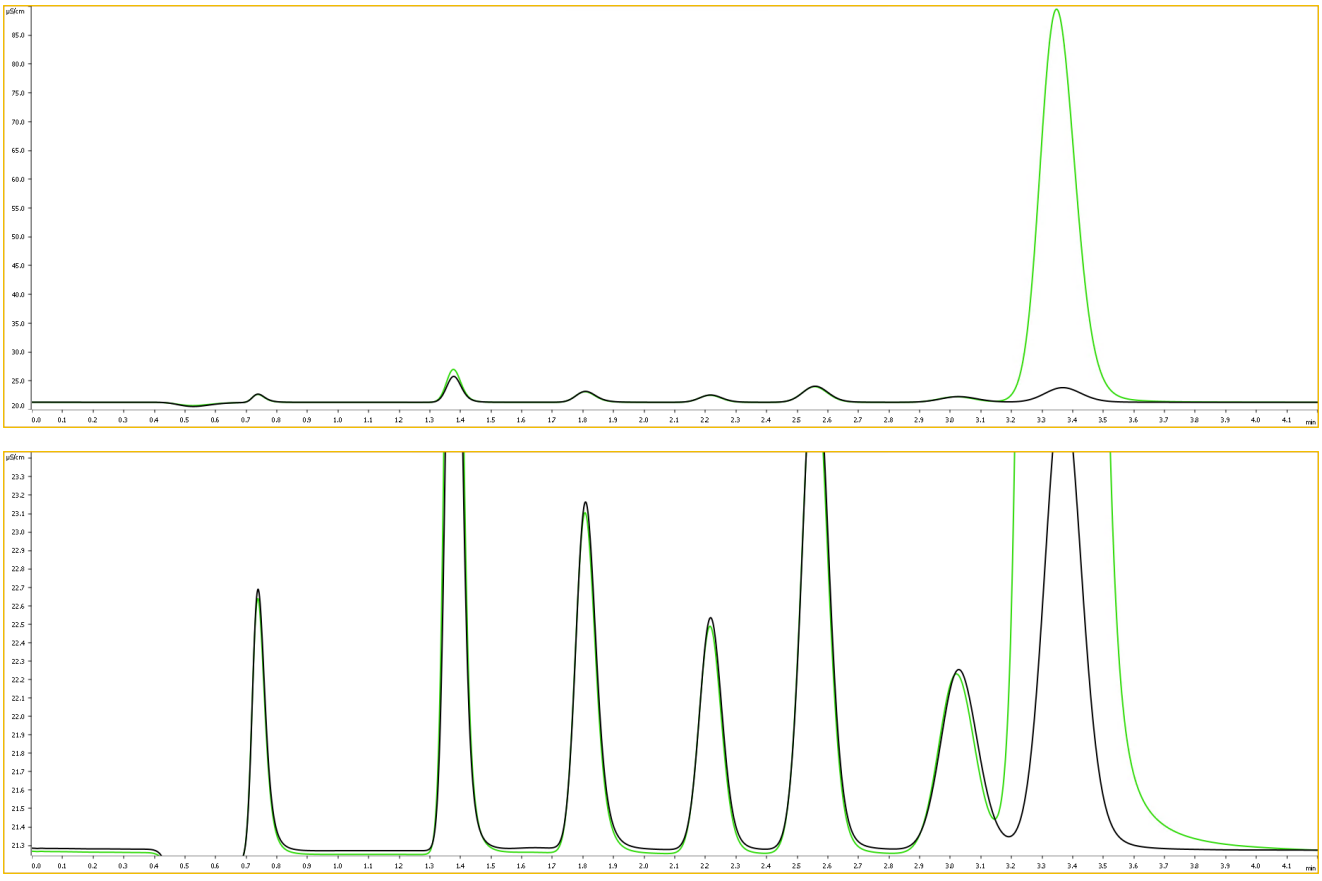


Figure 12. Overlay of artificial samples with different concentrations of sulfate (black: 10 mg/L; green: 200 mg/L).

6. Impact of carbonate on chromatogram

The overlay below shows the effect of carbonate in the sample on the separation performance. All peaks remain unchanged and are completely independent of the carbonate concentration, which elutes between chloride and nitrite. Since this system uses chemical suppression, the carbonate peak is visible as a broad peak.. Column overloading was not observed under the conditions shown (up to 300 mg/L bicarbonate.

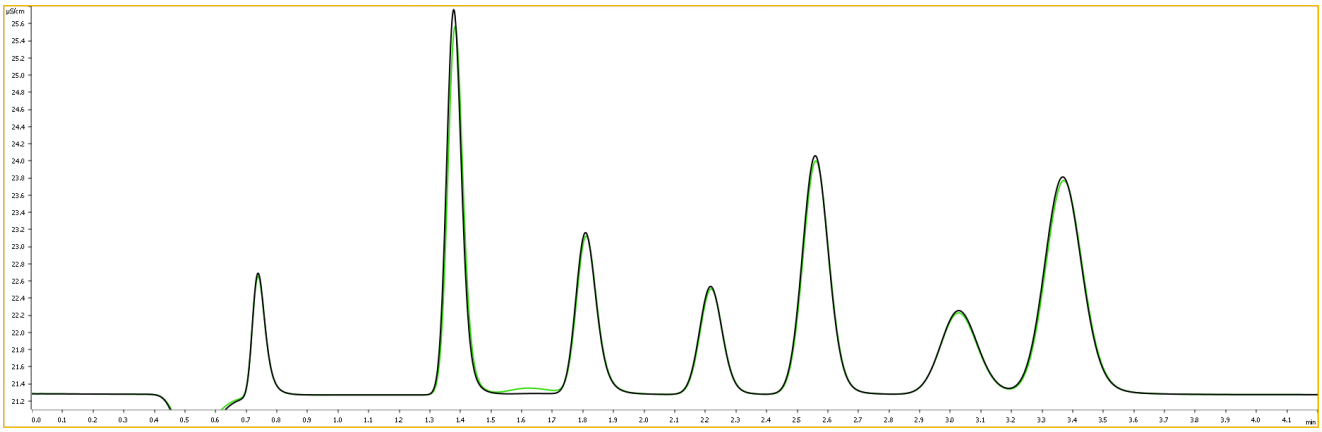


Figure 13. Overlay of artificial samples with different concentrations of carbonate (black: 0 mg/L; green: 300 mg/L).

7. Position of the early eluting organic acids

The chromatogram below shows the effect of early eluting, small molecular weight organic acids in the sample on the separation performance. Acetate (sample was slightly degraded, therefore giving little response only), and formate were added to the sample in a concentration of 1 mg/L. The elution order is fluoride, acetate, formate, chloride. Thereby, acetate does not disturb the determination of fluoride, and formate does not disturb the determination of chloride.

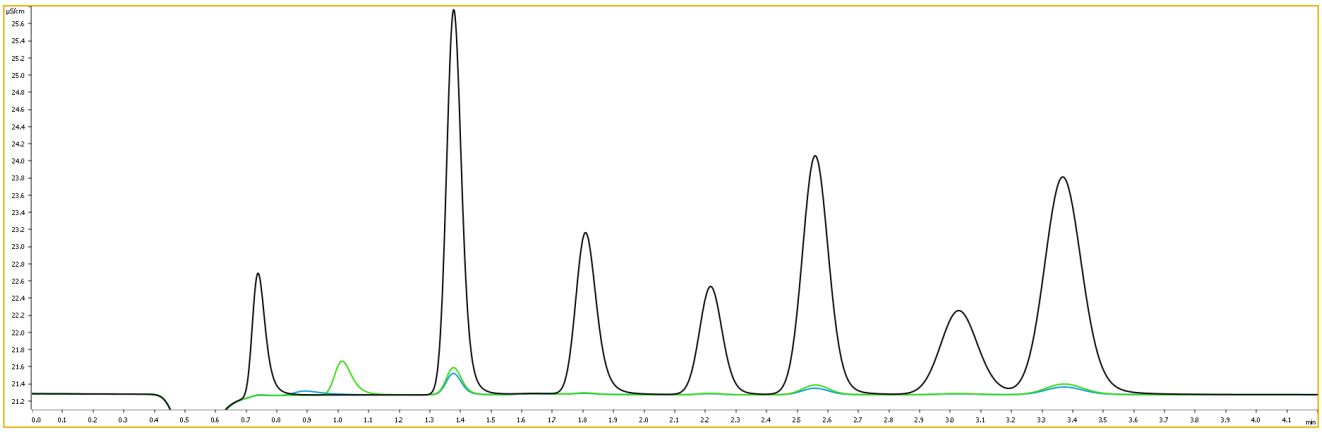


Figure 14. Overlay of artificial samples with (green and blue) and without (black) the early eluting organic acids at 1 mg/L.

8. Even faster analysis

The Metrosep A Supp 19 - 50/4.0 is released for flow rates up to 1.8 mL/min and even under these conditions, the separation of the standard anions is still possible. In that case, the analysis time is reduced by a third, meaning that the analysis of the 7 standard anions can be performed in less than 3 minutes. Keep in mind that under these accelerated conditions, the resolution will be slightly decreased. With the column used here, the resolution between phosphate and sulfate reduced from 1.43 at 1.2 mL/min to 1.30 at 1.8 mL/min in standard 4.

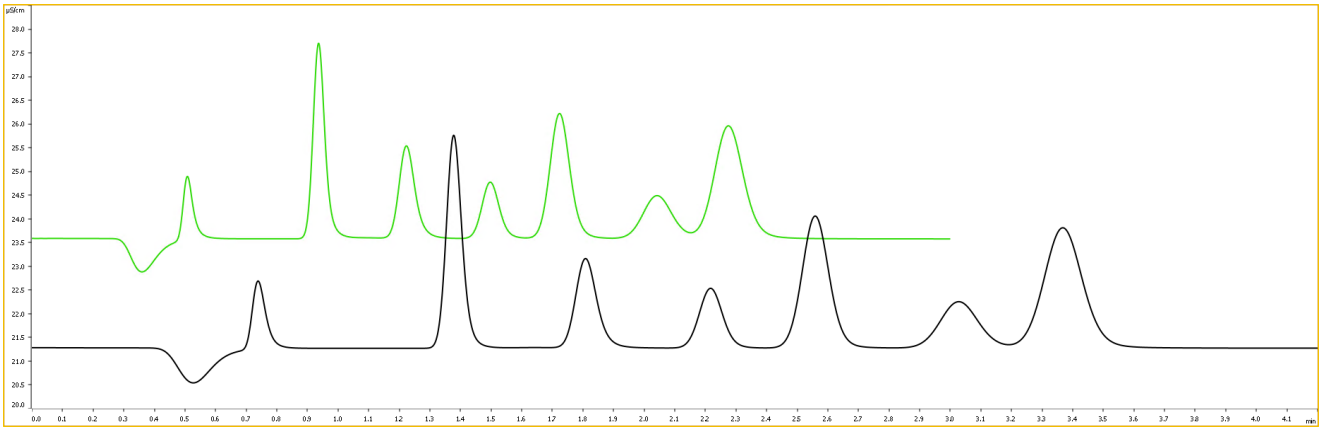


Figure 15. Overlay of standard 4 (1 mg/L fluoride, 5 mg/L chloride, nitrite and bromide, 10 mg/L nitrate, phosphate and sulfate) at 1.2 mL/min (black) and 1.8 mL/min (green).