Determination of anions in tap water using US EPA method 300

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In this white paper, the seven common anions (fluoride, chloride, nitrite, bromide, nitrate, phosphate and sulfate) required for US EPA method 300 Part A [1,2] were analyzed using a Metrohm ion chromatography system. The system was equipped with the optional Inline Ultrafiltration and an automated eluent production module.

Using optimized chromatographic conditions, baseline separation of all the seven ions is achieved in under 10 minutes using Metrosep A Supp 5 - 100/4.0. The economic benefits of automated ultrafiltration and eluent preparation are discussed in detail. The result of the method detection limit (MDL) study is also presented.

Introduction

In the US, the Environmental Protection Agency (EPA) establishes the Maximum Contamination Levels (MCL) in drinking water through the Safe Drinking Water Act (SDWA), and it regulates industrial discharge MCL through the Clean Water Act (CWA). A growing list of aqueous contaminants and increasingly stringent regulatory requirements require labs to process more samples in less time, without sacrificing accuracy. Ion chromatography (IC) is the EPA's established technique for the determination of concentration of common anions in water samples.

Metrohm

Determining ion concentrations in each unique sample requires careful selection of separation conditions, detection method and sample preparation. Use of automated sample preparation – including Inline Ultrafiltration – simplifies analysis, generates more accurate results and reduces total measurement time and labor in environmental labs.

Reagents

Sodium carbonate/bicarbonate 20x eluent concentrate
Sulfuric acid, CAS 7664-93-9
Ultrapure water, resistivity >18 MΩ·cm (25 °C)

Instruments

930 Compact IC Flex ChS	2.930.1200
IC Conductivity Detector	2.850.9010
800 Dosino	2.800.0010
919 IC Autosampler plus	2.919.0020
941 Eluent Production Module (EPM)	2.941.0010
IC Equipment: Dosino Regeneration	6.5330.190
IC Equipment: Inline Ultrafiltration	6.5330.110
MSM Rotor	6.2832.000
MSM Rotor Adapter	6.2842.020
10 µL PEEK Sample Loop	6.1825.230
MagIC Net Compact	6.6059.311
Metrosep A Supp 5 - 100/4.0	6.1006.510
Metrosep A Supp 4/5 Guard/4.0	6.1006.500

Solutions

Eluents	3.2 mmol/L Na_2CO_3 + 1.0 mmol/L $NaHCO_3$
Regenerant	500 mmol/L H_2SO_4 + STREAM

Samples

Tampa tap water

Standards

Standards were prepared using a 100 mg/L mixed standard. A 2 mg/L stock standard was manually prepared and then diluted to create a 6 point calibration.

In ultrapure water (mg/L)	S1	S2	S3	S4	S5	S6
Fluoride	0.04	0.10	0.25	0.50	1.00	2.00
Chloride	0.04	0.10	0.25	0.50	1.00	2.00
Nitrite	0.04	0.10	0.25	0.50	1.00	2.00
Bromide	0.04	0.10	0.25	0.50	1.00	2.00
Nitrate	0.04	0.10	0.25	0.50	1.00	2.00
Phosphate	0.04	0.10	0.25	0.50	1.00	2.00
Sulfate	0.04	0.10	0.25	0.50	1.00	2.00

IC Parameters

Eluent flow	0.8 mL/min
Column temperature	Ambient
Degasser	n/a
MCS	n/a
Sample loop	10 µL
MSM regenerant	500 mmol/L sulfuric acid
MSM rinsing	STREAM
MSM	Automatic Stepping
Recording time	10 min
Background conductivity	12-20 µS/cm
Noise	<0.15 nS/cm

Calculation

Automatic integration with MagIC Net 3.1 software using peak area for all analytes.

Results and discussion

In this application work, seven anions were separated on a Metrosep A Supp 5 - 100/4.0 column using 3.2 mmol/L sodium carbonate/1.0 mmol/L sodium bicarbonate eluent followed by chemical suppression and conductivity detection. The suppressor was regenerated using 500 mmol/L sulfuric acid and then rinsed with the water from conductivity detector. The column used here offers baseline separation of the anions. The MSM suppressor provides fast equilibration.

Heavy metals like iron, which are often present in environmental water, accumulate in the suppressor, but can be removed using a regenerant solution containing oxalic acid. This process provides stable and consistent performance for environmental samples. Complete chemical regeneration ensures a very low noise and high sensitivity. As a result, detection limits can be achieved with lower sample injection volumes increasing column life. The Metrohm suppressor is well suited for any environmental lab with low, medium or heavy sample load.

Eluent preparation

The Metrohm 941 Eluent Production Module (EPM) was used to prepare the eluent. Commercially available 20x eluent concentrate was used for this study. Customer-prepared eluent concentrates can also be used. The EPM provides the ability to change eluent concentrates without downtime and long equilibration time typically encountered when using proprietary eluent cartridges. The EPM ensures consistent retention times compared to the manually prepared eluent.

Sample filtration

Samples measured using EPA 300 require filtration to protect the flow path and IC columns. The common method of automated sample filtration requires filter caps. However, filter caps have 20 µm pore size and do not remove smaller particles. These particles are deposited on the analytical column, reducing its longevity.

Syringe filters are effective in removing particulate, however, they are expensive and labor intensive.

Metrohm Inline Ultrafiltration uses commercially available 0.2 µm pore size filters that provide filtration of 200 - 300 samples using a single filter with less than 0.1% carry over.

Calibration

A calibration ranging from 0.04 mg/L to 2.0 mg/L for all seven anions was performed using the 2.0 mg/L stock standard.

Analyte	Range (mg/L)	RSD (%)	Corr. Coeff.
Fluoride	0.04 – 2.0	0.210070	0.999999
Chloride	0.04 – 2.0	0.902796	0.999982
Nitrite	0.04 – 2.0	1.725342	0.999935
Bromide	0.04 – 2.0	0.442065	0.999999
Nitrate	0.04 – 2.0	0.921694	0.999981
Phosphate	0.04 – 2.0	1.266553	0.999965
Sulfate	0.04 – 2.0	0.500772	0.999994

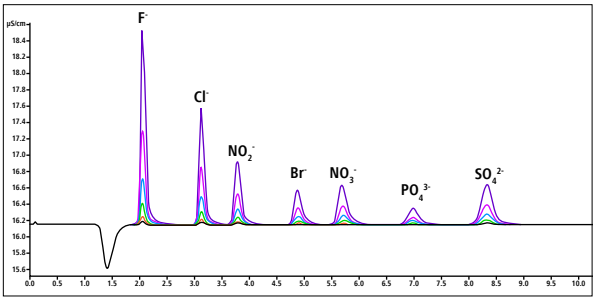

Figure 1. Overlay of calibration standards

Figure 1 shows the overlay of the 6 calibrations with excellent linearity; correlation coefficient (>0.9999) and relative standard deviations (RSD < 2%).

In order to demonstrate the difference in run times, the standards were also run at a flow rate of 0.7 mL/min and an overlay of chromatograms from standard 5 (1 mg/L) at 0.7 & 0.8 mL/min is shown in figure 2.

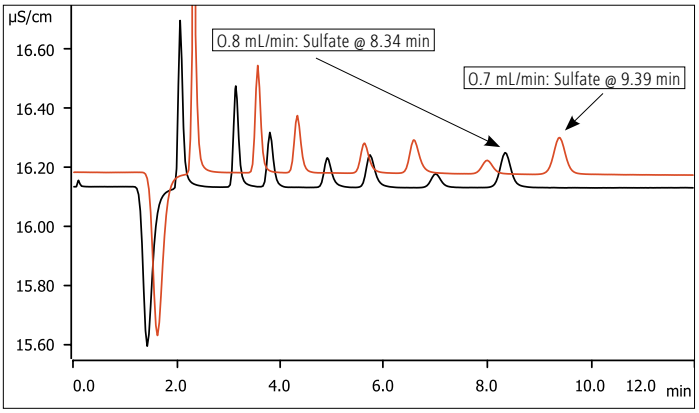

Figure 2: Overlay of 1 mg/L at 0.7 mL/min & 0.8 mL/min flow rate

Sample analysis

A set of 10 tap water samples were manually diluted 1:100 and measured over a 3-day period for a total of 30 analyses. An overlay of chromatograms for the 3-day study is shown in figure 3. The results showed chloride levels around 23 mg/L, nitrate near 5.9 mg/L and sulfate around 92 mg/L. A table of average concentration, standard deviation and relative standard deviation for all 30 runs is shown below.

Tap water (n=30)	Chloride	Nitrate	Sulfate
Average (mg/L)	23.19	5.89	92.42
Standard deviation (mg/L)	0.37	0.31	6.50
RSD (%)	1.59	5.27	7.03

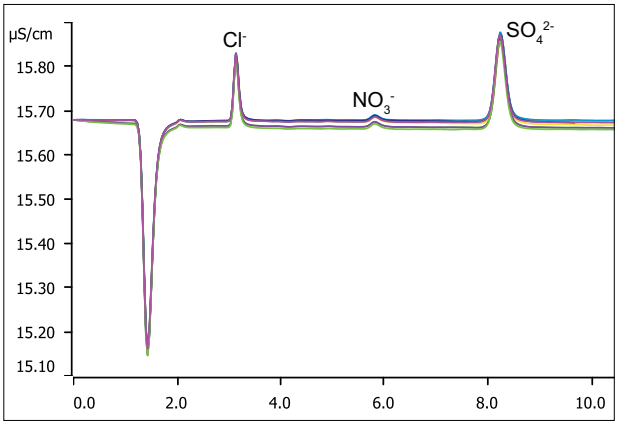

Figure 3: Overlay of ten chromatograms for tap water

Method detection limit & limit of quantitation

A method detection limit study was performed by analyzing a set of 7 replicates of 0.04 mg/L mixed standard over a 3-day period. The MDLs were calculated by multiplying the standard deviation (n=7) and the t-test factor, 3.14. The limit of quantitation (LOQ) was also calculated for all the anions as 10 times the standard deviation of the 7 replicates. The results of the MDL and LOQ study are presented in table 1.

The daily calculated MDLs showed only minimal variations during the 3-day study. All the MDL values comply with the requirements of 40 CFR Part 136 Appendix B and EPA methods 300.0 & 300.1.

	Day 1			Day 2			Day 3		
	Mean (mg/L)	MDL (mg/L)	LOQ (mg/L)	Mean (mg/L)	MDL (mg/L)	LOQ (mg/L)	Mean (mg/L)	MDL (mg/L)	LOQ (mg/L)
Fluoride	0.038	0.009	0.028	0.038	0.009	0.030	0.039	0.006	0.018
Chloride	0.037	0.006	0.018	0.038	0.004	0.014	0.046	0.005	0.016
Nitrite	0.040	0.008	0.026	0.036	0.008	0.026	0.038	0.006	0.020
Bromide	0.037	0.010	0.032	0.038	0.005	0.015	0.042	0.005	0.017
Nitrate	0.037	0.008	0.026	0.038	0.010	0.033	0.045	0.006	0.021
Phosphate	0.042	0.022	0.071	0.041	0.018	0.056	0.044	0.015	0.049
Sulfate	0.039	0.008	0.025	0.039	0.009	0.029	0.045	0.005	0.017

Table 1: Summary of MDL/LOQ study Data for 7 anions

Conclusion

The Metrohm IC system used in this study is capable of meeting the requirements for the seven anions listed under part A of EPA methods 300.0 & 300.1. The calculated MDLs fully comply with the requirements of the EPA methods and 40 CFR Part 136 Appendix B. The Inline Ultrafiltration feature used in the study streamlines sample preparation, increases productivity and therefore profitability of any lab running the EPA 300 method. The 941 Eluent Production Module provides a simple and inexpensive solution to the routine task of eluent preparation leading to greater reliability and accuracy.

References

1. EPA Method 300.0 Determination of inorganic anions by ion chromatography

2. EPA Method 300.1 Determination of inorganic anions in drinking water by ion chromatography Revision 1.0

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