

Fast Analysis of Anions in Drinking Water by Ion Chromatography

INTRODUCTION

The U.S. National Primary Drinking Water Standards specify a Maximum Contaminant Level (MCL) for a number of inorganic anions, including fluoride, nitrite, and nitrate. The MCLs are specified to minimize potential health effects arising from ingestion of these anions in drinking water. Other common anions, such as chloride and sulfate, are considered secondary contaminants and guidelines exist regarding taste, odor, color, and certain aesthetic effects. U.S. EPA Method 300.0¹ describes the use of ion chromatography (IC) with a Dionex IonPac[®] AS4A anion exchange column, a carbonate/bicarbonate eluent, and suppressed conductivity detection for the determination of these inorganic anions in environmental waters, such as drinking water, wastewater, and aqueous soil extracts. The scope of the method allows optional columns and suppression devices to be used provided that comparable resolution of peaks is obtained and the method quality control requirements can be met.

In this paper, we describe the use of the IonPac AS14A anion exchange column² with a new Atlas[™] Electrolytic Suppressor (AES[™])³ for the routine high-throughput determination of common inorganic anions in drinking water matrices. The IonPac AS14A provides

greater speed and efficiency, ruggedness equivalent to the AS4A-SC column, improved separation of fluoride from the void volume (water dip), and better overall separation selectivity. The AES is a continuously electrolytically regenerated suppressor based on the MonoDisc[™] suppression technology. The Atlas electrolytic suppressor offers lower baseline noise and improved ruggedness and reliability. The analytical throughput, potential interferences, linear range, method detection limits, system stability, and analyte recoveries obtained using the AS14A column with the Atlas suppressor for drinking water are described in this Application Note.

EQUIPMENT

Dionex DX-600 ion chromatography system configured for Atlas anion suppression consisting of:

GS50 or GP50 Gradient Pump

ED50A Electrochemical Detector or CD25A
Conductivity Detector

AS40 Automated Sampler with 0.5-mL sample vials

LC30 Chromatography Oven with a rear-loading valve

PeakNet[®] Chromatography Workstation

REAGENTS AND STANDARDS

Deionized water (DI H₂O), Type I reagent grade, 18 M Ω -cm resistance or better
AS14A Eluent Concentrate (100X), P/N 056937
All anion standards were 99% ACS reagent grade or better:
Sodium fluoride, CAS 7681-49-4 (Fisher Scientific or other)
Sodium chloride, CAS 7647-14-5 (J.T. Baker or other)
Sodium nitrite, CAS 5347-50-0 (Fisher Scientific or other)
Sodium bromide, CAS 7647-15-6 (EM Sciences or other)
Sodium nitrate, CAS 7631-99-4 (Aldrich Chemical Company or other)
Potassium phosphate, monobasic, anhydrous, CAS 7778-77-0 (Sigma Chemical Company or other)
Sodium sulfate, anhydrous, CAS 7757-82-6 (EM Sciences or other)

CONDITIONS

Columns: IonPac AS14A Analytical, 3 x 150 mm, 5- μ m particle diameter (P/N 056901)
IonPac AG14A Guard, 3 x 30 mm, 5- μ m particle diameter (P/N 056899)
Eluent: 8.0 mM Sodium carbonate and 1.0 mM sodium bicarbonate
Temperature: 30 °C
Run Time: 6 min
Flow Rate: 0.8 mL/min
Sample Volume: 25 μ L
Detection: Suppressed conductivity, Atlas AAES™ (P/N 056116), recycle mode, 45 mA
System
Backpressure: 2610–2890 psi (18–20 MPa)
Background
Conductance: 23–25 μ S

PREPARATION OF SOLUTIONS AND REAGENTS

Standard Solution

Starting Anion Standard Solution (10,000 mg/L)

Sodium fluoride—Formula weight = 42.00, anionic mass percent = 45.26%. Dissolve 2.209 g of sodium fluoride solid in 100 mL deionized water.
Sodium chloride—Formula weight = 58.45, anionic mass percent = 60.67%. Dissolve 1.648 g of sodium chloride solid in 100 mL deionized water.
Sodium nitrite—Formula weight = 69.00, anionic mass percent = 66.68%. Dissolve 1.500 g of sodium nitrite solid in 100 mL deionized water.
Sodium bromide—Formula weight = 102.91, anionic mass percent = 77.66%. Dissolve 1.288 g of sodium bromide solid in 100 mL deionized water.
Sodium nitrate—Formula weight = 85.01, anionic mass percent = 72.96%. Dissolve 1.371 g of sodium nitrate solid in 100 mL deionized water.
Potassium phosphate (monobasic)—Formula weight = 136.09, anionic mass percent = 71.27%. Dissolve 1.403 g of potassium phosphate solid in 100 mL deionized water.
Sodium sulfate—Formula weight = 142.06, anionic mass percent = 83.82%. Dissolve 1.193 g of sodium sulfate solid in 100 mL deionized water.

Stock Anion Standard Solution (1000 mg/L)

Dilute each 10,000 mg/L starting anion solution 10-fold in deionized water.

Working Standard Solutions

Dilute 1000 mg/L stock anion standard solutions together as required with deionized water to prepare the appropriate working standard mixtures. The five levels of working standards used in this study for calibration and quality checks are presented in Table 1. These concentration ranges were chosen to bracket the concentrations typical for drinking water samples. The intermediate standard (level 3) was used as a quality check and to evaluate long-term response stability.

LABORATORY FORTIFIED BLANK (LFB) AND MATRIX (LFM)

Dilute 1000 mg/L standard solutions together as required with deionized water to prepare 20X fortification concentrate (see Table 1). The 20X fortification concentrate (5.0 mL) was diluted in deionized labora-

tory water (95.0 mL) to produce the LFB, and 5.0 mL was added to 95.0 mL of Sunnyvale, California drinking water to make the LFM. The concentrations of LFB and LFM are given in Table 1. The LFB and LFM are used to calculate the spike recovery of anions from deionized water and drinking water.

Table 1 Anion Standards and Controls									
	Anion Standards,* mg/L (ppm)					LFB*	LFM**		
	Levels							DI Water Blank Fortification (ppm)	Matrix Fortification (ppm)
	1	2	3	4	5				
Fluoride	0.1	0.5	2.5	5	10	1	1		
Chloride	0.5	5	25	50	100	10	10		
Nitrite	0.1	1	5	10	20	2	2		
Bromide	0.1	1	5	10	20	2	2		
Nitrate	0.1	1	5	10	20	5	5		
Phosphate	0.2	1.5	7.5	15	30	10	10		
Sulfate	0.5	5	25	50	100	20	20		

25- μ L Injections

LFB = Laboratory fortified blank

LFM = Laboratory fortified matrix

* Anion standards and LFBs were prepared in laboratory water.

** LFM were prepared in tap water collected from Sunnyvale, California.

Eluent Solution

8.0 mM Sodium Carbonate/1.0 mM Sodium Bicarbonate

Weigh 1980 g deionized water into an eluent bottle. Degas water for approximately 20 min. Carefully add 20.0 mL of the AS14A Eluent Concentrate (100X) to the degassed water. Mix and then quickly transfer the eluent bottle to the instrument and pressurize the bottle with helium at 8 psi (0.055 MPa). For experiments involving stability studies longer than 1 day, the eluent was prepared as described above but added to the previous eluent.

RESULTS AND DISCUSSION

The use of the IonPac AS14A (3 mm) column at 0.8 mL/min can reduce the run time to 6 minutes (Figure 1) from the usual 10 min for the 0.5 mL/min flow rates. The run times for other IonPac columns commonly used for drinking water analysis are presented in Table 2. Actual run times are typically longer because additional time is needed to fill the injection loop of the autosampler prior to injection and to download data. This additional time varies with the autosampler used. The run times can be reduced by several means: increased eluent strength,

increased temperature, and increased flow rate. The AS4A operated at 2 mL/min can reduce the run times to 9 min, but cannot completely resolve the fluoride peak from the water dip. The AS14 column was designed to elute fluoride away from the water dip, but the run times are longer. The AS14A (3 mm) column was designed to elute fluoride from the water dip and also reduce the run times. The performance of this column is maintained

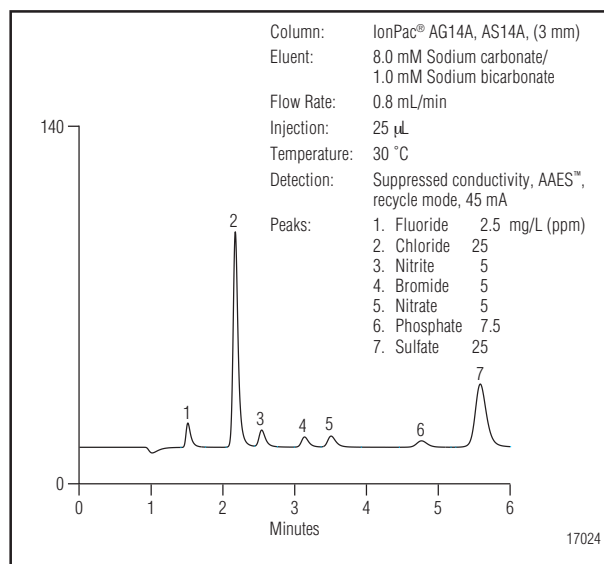


Figure 1. Seven common anion standards using the AS14A (3 mm) at 0.8 mL/min with the AAES suppressor.

Table 2 Comparison of Run Times and Throughput for Dionex IonPac Columns Recommended for Drinking Water Analysis

Column Set	Flow Rate (mL/min)	Sodium Carbonate/Sodium Bicarbonate Eluent Concentration (mM)	Run Time (min)*	Actual Run Time (min)**	No. of Inject. per 24 h
AS4A/AG4A (4 mm)	2.0	1.8 mM/1.7 mM	9	10.1	143
AS14/AG14 (4 mm)	1.2	3.5 mM/1.0 mM	14	15.1	95
	1.2	4.8 mM/0.6 mM	11	12.1	119
	1.5	4.8 mM/0.6 mM	9	10.1	143
	2.0	4.8 mM/0.6 mM	7	8.1	178
AS14A/AG14A (3mm)	0.5	8.0 mM/1.0 mM	10	11.1	130
	0.8	8.0 mM/1.0 mM	6	7.1	203

* Time from injection to end of shoulder of last peak (sulfate) plus -1 min

** Actual time per injection, which includes AS40 autosampler loading, injection, and data transfer.

even at higher flow rates, making it well suited for high-throughput water analysis. Using the AS40 autosampler, each injection was calculated to take 7.1 minutes of actual time, and therefore 203 injections were possible over 24 h, surpassing the throughput of any other IonPac column (see Table 2).

The Atlas suppressor is appropriate for this application. Although the Atlas has lower capacity than the ASRS® and AMMS® membrane-based suppressors, the relatively low ionic strength of the carbonate eluent used in this application is well within its operating range. The advantage of Atlas suppression is that baseline noise can be minimized relative to the membrane suppression. In the Recycle mode, the Atlas suppressor provides both low noise and the convenience of long-term maintenance-free operation. An equilibrated system will produce peak-to-peak noise between 0.50–3.5 nS for this application. Figure 2 compares baseline noise between ASRS-ULTRA and Atlas suppressors. The magnitude of the baseline noise can be further reduced by using the External Water mode of suppression as in membrane-based suppressors. All results presented in this Note used the Recycle mode. Both the ASRS-ULTRA and the Atlas suppressor can be used for this high throughput application using the AS14A at higher flow rates, but the Atlas generally produces lower noise and thus lower detection limits.

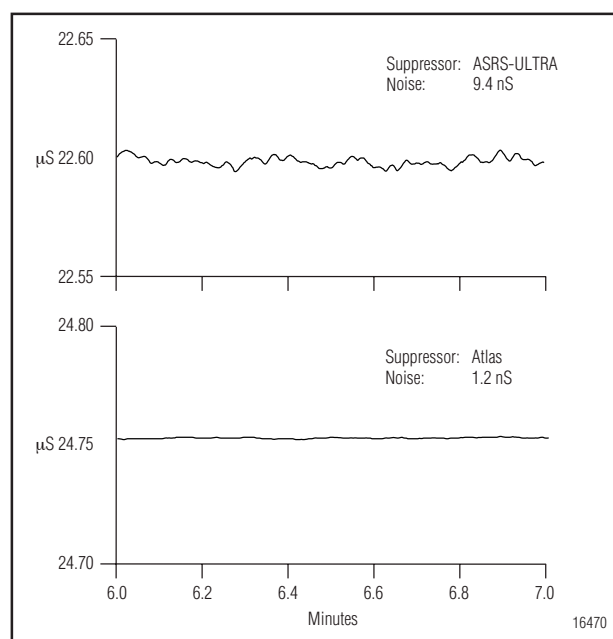


Figure 2. Baseline noise for ASRS and Atlas suppressors using the IonPac AS14A (3 mm) at 0.8 mL/min (8 mM Sodium carbonate and 1 mM sodium bicarbonate eluent).

4 Fast Analysis of Anions in Drinking Water by Ion Chromatography

Because the Atlas suppressor produces lower noise, the limits of detection (LOD) and quantitation (LOQ) are reduced. Table 3 compares the estimated LODs and LOQs of seven anions for both ASRS-ULTRA and Atlas suppressors. The LOD is defined in this Note as the corresponding concentration of each respective standard anion peak height that is equivalent to three times the average of 40 one-minute interval peak-to-peak noise measure. The LOQ is ten times this average. The LOD for the Atlas ranged from 0.8–10 ppb, and from 6–74 ppb for the ASRS-ULTRA. In this study, the Atlas had about a seven times lower detection limit for each anion. Noise values will vary with each suppressor and will affect this comparison. In general, Atlas suppressors should yield lower detection limits than ASRS suppressors.

Table 3 Lower Limits of Detection and Quantification Using the AS14A (3 mm) at 0.8 mL/min with ASRS and Atlas Suppression				
	Lower Limits of Detection (LOD)* (ppb)		Lower Limits of Quantification (LOQ)** (ppb)	
	ASRS	Atlas	ASRS	Atlas
Fluoride	6	0.8	20	3
Chloride	7	1	24	3
Nitrite	20	3	68	9
Bromide	29	4	95	13
Nitrate	24	4	82	12
Phosphate	74	10	245	32
Sulfate	25	3	83	10

* LOD based on 3 times the peak-to-peak noise.

** LOQ based on 10 times the peak-to-peak noise.

The lower detection limits using Atlas suppression permit the detection of trace anions in drinking water. Figure 3 shows the separation of anions in Sunnyvale, CA drinking water using the AS14A (3 mm) column at 0.8 mL/min with Atlas suppression. Bromide was measured at a concentration of 20 ppb in this drinking water and the LOD for this ion was 4 ppb, which is above the measured concentration of this drinking water sample based on the Atlas results. The measure of bromide at this concentration is often difficult to achieve by other methods.

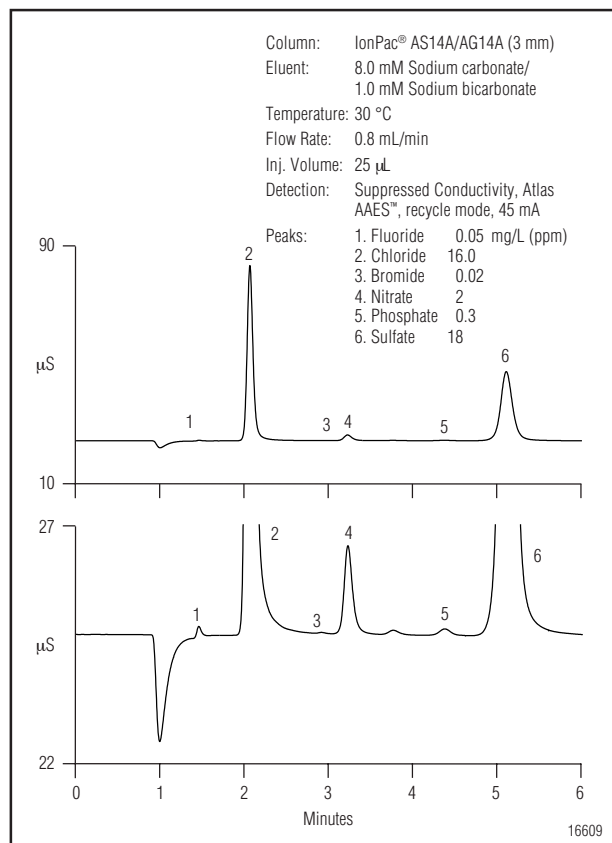


Figure 3. Anions in Sunnyvale, CA drinking water in August separated using the IonPac® AS14A (3 mm) at 0.8 mL/min.

Peak area precision generally improves at higher concentrations. Sunnyvale drinking water was analyzed sequentially for over 6 days in groups of 20 injections interspersed with duplicate quality control samples (blank, level 3 standard, LFB, LFM). The measured anion concentrations for the 940 injections of drinking water sample were plotted with the calculated RSDs (Figures 4 and 5). Chloride (17 ppm) and sulfate (19 ppm) concentrations were measured with high precision (1.2 and 1.1% RSD, respectively). At low to trace level concentrations, high stability was also observed. Nitrate (1.9 ppm) was 1.2% RSD, phosphate (0.33 ppm) was 4.9% RSD, fluoride (0.047 ppm) was 5.5%, and bromide (0.021 ppm) was 14% RSD. This measured concentration of bromide (21 ppb) was only slightly higher than the lower limit of quantification (13 ppb) for this anion using the Atlas (Table 3), thus the precision was poor. When ASRS-ULTRA suppression is used under these conditions, the precision decreases for anions close in concentration to the LOD (Table 4).

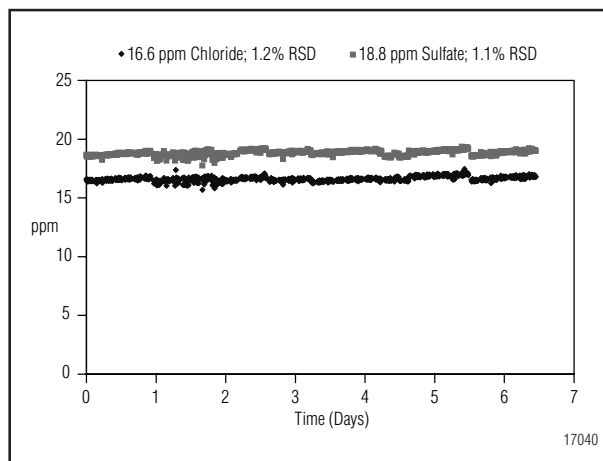


Figure 4. Stability of high level anions in Sunnyvale, CA drinking water using the AS14A (3 mm) at 0.8 mL/min with the Atlas suppressor.

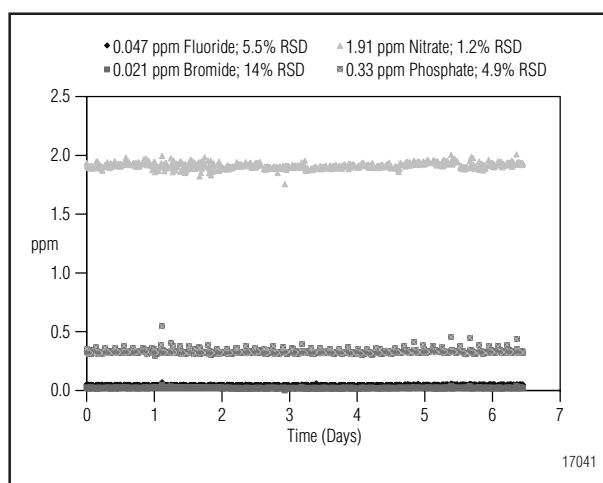


Figure 5. Stability of low level anions in Sunnyvale, CA drinking water using the AS14A (3 mm) at 0.8 mL/min with the Atlas suppressor.

Table 4 Peak Area Precision for the Same Sunnyvale Water Sample Over 3 Days Using ASRS and Atlas Suppressors			
	Measured Concentration (ppm)	RSD	
		ASRS %	Atlas %
Fluoride	0.05	21.0	5.1
Chloride	17	1.0	1.1
Nitrite	< 0.003	ND	ND
Bromide	0.02	ND	14.0
Nitrate	2	1.2	1.2
Phosphate	0.3	7.3	5.0
Sulfate	19	0.9	1.1

ND = Not Detected (< 50% of the injections below the detection limit)
 IonPac® AS14A and AG14A (3 mm) at 0.8 mL/min, 25 µL injections

The r^2 values ranged from 0.997 to 1.000 for the seven anions (Figure 6). Linearity extends above the concentrations selected for this study and presented in this Application Note. These concentrations used for calibration were designed to appropriately encompass the concentrations typically observed in drinking water samples. The response factors for each anion were calculated from the ratio of peak area to ppm concentration for a 25- μ L injection. The response for each anion remained stable over 6 days of continuous operation (Figure 7), with RSDs ranging from 1.0 to 2.3%.

The recovery of anions from either deionized water (LFB) or drinking water (LFM) was calculated using the calibration curve generated at the beginning of the study and remained high over 6 days of continuous operation. The mean % recovery ranged from 96–103% for the LFB, and 92–102% for the LFM (Table 5). At no time did the percent recovery for the LFB drop below the 90% threshold for U.S. EPA Method 300.0, nor did the recovery from LFM drop below the 80% threshold. The retention times remained stable for all anions over 6 days of continuous operation, with RSDs ranging from 0.4–0.9%. At 4.5 days, a slight shift in retention time was observed corresponding in time with the replenishment of an eluent bottle, indicating some interday variance in retention times might occur from minor variations in eluent preparation. The optimized settings for the retention time acceptance window in the PeakNet software and the high level of separation of anions prevented misidentification of peaks.

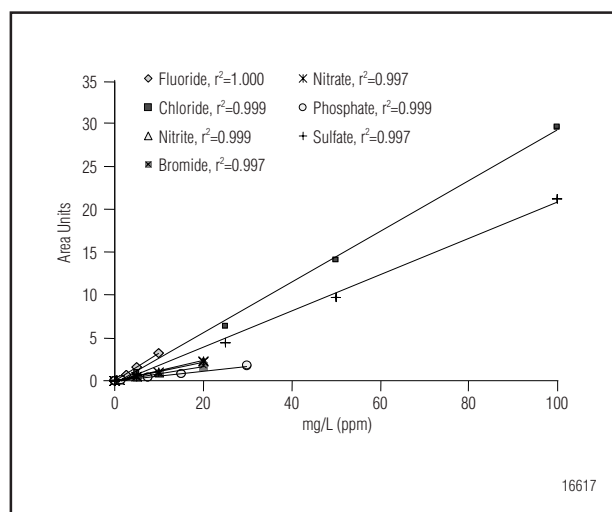


Figure 6. Calibration curves for common anions using the AS14A (3 mm) at 0.8 mL/min with the Atlas suppressor.

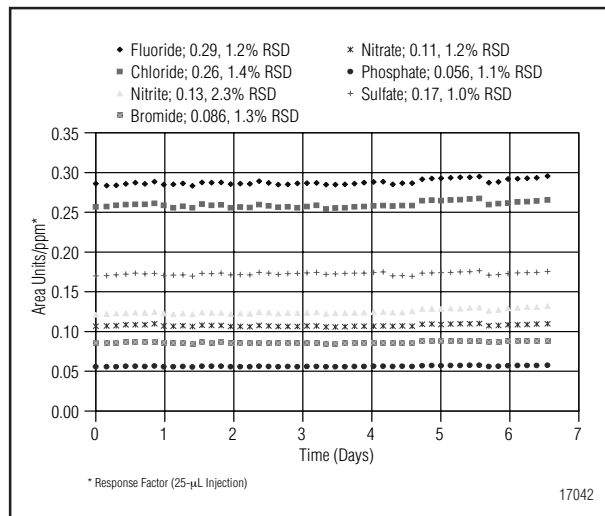


Figure 7. Stability of peak area response factors over 6 days using the AS14A (3 mm) at 0.8 mL/min with the Atlas suppressor.

Table 5 Recoveries of Common Anions From Deionized Lab Water (LFB) and Drinking Water Sample Matrix (LFM) Over 6 Days Using the AS14A (3 mm) at 0.8 mL/min with the Atlas Suppressor

Anion	Recovery			
	LFB		LFM	
	Mean%	RSD%	Mean%	RSD%
Fluoride	96	1.1	97	1.2
Chloride	99	1.4	98	2.8
Nitrite	98	2.5	92	3.2
Bromide	98	1.3	98	1.4
Nitrate	102	1.0	97	1.2
Phosphate	98	1.0	99	1.0
Sulfate	103	0.9	102	1.7

This method is useful for a variety of drinking water samples. Figures 8 and 9 show the separation of anions from fluorinated drinking water (Palo Alto, CA) and from Sierra Nevada mountain water low in ions (Twain Harte, CA), respectively. Even at high fluoride levels, this peak continues to elute out of the water dip using the AS14A (3 mm) column at 0.8 mL/min. When concentrations of ions become low, the use of Atlas suppression makes the detection of trace ions possible and with greater precision and accuracy. Figures 3 and 10 show water collected from the same Sunnyvale source during different seasons (August and February, respectively). Table 6 summarizes the measured results for the water samples tested and shows that this method is capable of monitoring seasonal changes in drinking water anions.

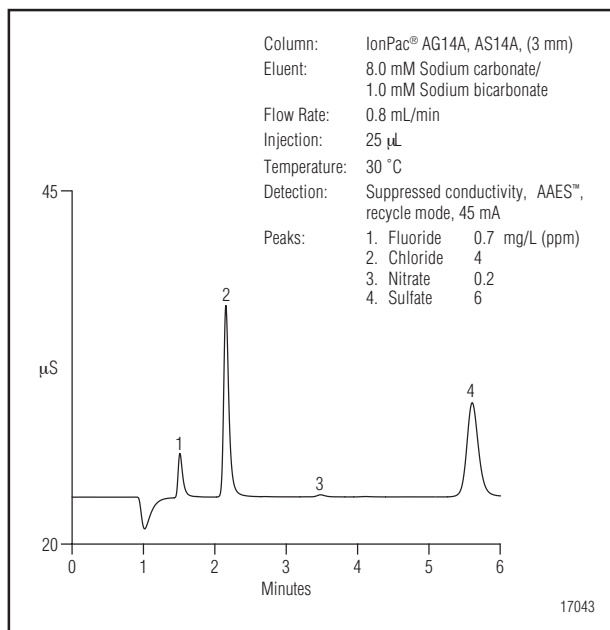


Figure 8. Anions in Palo Alto, CA drinking water separated using the IonPac AS14A (3 mm) at 0.8 mL/min.

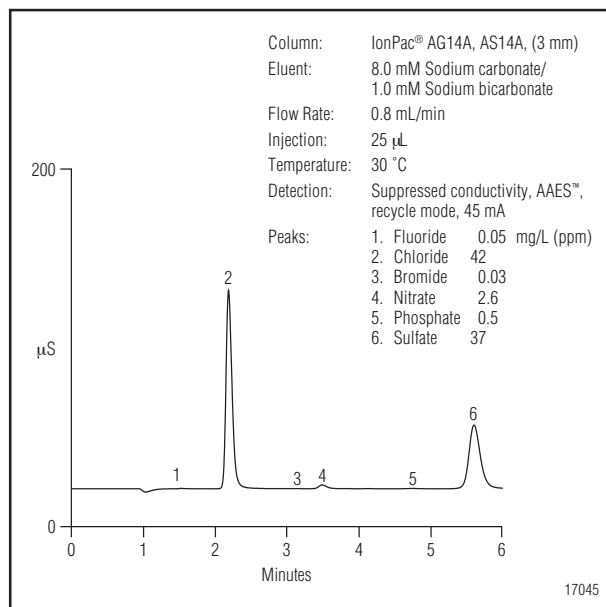


Figure 10. Anions in Sunnyvale, CA drinking water in February separated using the IonPac AS14A (3 mm) at 0.8 mL/min.

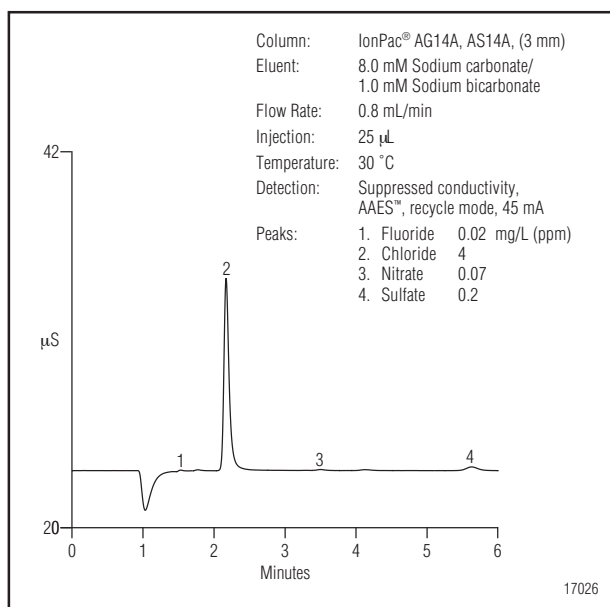


Figure 9. Anions in Twain Harte, CA drinking water separated using the IonPac AS14A (3 mm) at 0.8 mL/min.

	Sunnyvale 8/8/00 (ppm)	Sunnyvale 2/22/01 (ppm)	Palo Alto 2/21/01 (ppm)	Twain Harte 2/20/01 (ppm)
Fluoride	0.047	0.052	0.728	0.016
Chloride	16.6	42.1	4.1	3.5
Nitrite	< 0.003	< 0.003	< 0.003	< 0.003
Bromide	0.021	0.033	<0.004	<0.004
Nitrate	1.91	2.60	0.17	0.066
Phosphate	0.328	0.483	<0.010	<0.010
Sulfate	18.8	36.8	6.45	0.228

SUMMARY

The IonPac AS14A (3 mm) used at a faster flow rate reduces run times and increases sample throughput. The increase in flow rate from 0.5 to 0.8 mL/min increased the number of injections per day by 56%. The Atlas suppressor lowers baseline noise, which lowers detection limits and therefore improves the detection of trace-level ions. Good long-term performance was realized using the AS14A with Atlas suppression at 0.8 mL/min.

REFERENCES

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3. Small, H.; Riviello, J. "Electrically Polarized Ion-Exchange Beds in Ion Chromatography: Ion Reflux." *Anal. Chem.* **1998**, 70 (11), 2205-2212.

SUPPLIERS

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* Designed, developed, and manufactured under an NSAI registered ISO 9001 Quality System.



LPN 1295 5M 7/01
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