

Environmental

Fast analyses of anions in water with microbore columns using a compact ion chromatography system for reduced eluent use

Authors

Yukiko Kawahara, Neil Rumachik
Thermo Fisher Scientific
Sunnyvale, CA

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Introduction

In recent years, the growing awareness of environmental sustainability has compelled industries to seek methods that not only deliver high analytical performance but also minimize ecological impact. A crucial aspect of advancing towards green chemistry is the reduction of toxic waste produced during analytical processes. In ion chromatography (IC), lowering the eluent use and reducing analysis time are among the key strategies to minimize the environmental footprint.

This application note details the benefits of employing microbore columns in IC for the analysis of anions in water. Microbore columns, with diameters of 2 mm or less, require significantly lower eluent flow rates compared to standard bore (4 mm) columns. This presents a compelling solution to reduce eluent usage and thereby markedly decrease the volume of hazardous waste generated. Furthermore, we have achieved analysis times of under 10 minutes, increasing the analysis throughput while reducing total eluent consumption.

By incorporating microbore columns, laboratories can perform anion analysis with a substantially reduced environmental footprint. This approach aligns with the increasing global demand for greener analytical practices, ensuring that water quality monitoring is conducted more responsibly.

For this experiment, we selected a 250 mm column due to its higher capacity for analyzing a wide range of water types, including wastewater. For even faster analysis of cleaner water, a shorter 150 mm column may be considered.¹

Experimental

Equipment

- Thermo Scientific™ Dionex™ Inuvion™ IC System equipped with integrated regenerant pump and optional column heater (P/N 22185-60104)
- Thermo Scientific™ Dionex™ AS-AP Autosampler (P/N 074921)
- Optional Thermo Scientific™ Dionex™ VP Vacuum Pump Kit for Carbonate Removal (P/N 066463)

Software

Thermo Scientific™ Chromeleon™ Chromatography Data System (CDS) software version 7.3.2 or later

Consumables

- Thermo Scientific™ Dionex™ IonPac™ AS22 Analytical Column 2 × 250 mm (P/N 064137)
- Thermo Scientific™ Dionex™ IonPac™ AG22 Guard Column 2 × 50 mm (P/N 064135)
- Thermo Scientific™ Dionex™ ACRS 500 Chemically Regenerated Suppressor (2 mm) (P/N 085091) or Thermo Scientific™ Dionex™ ADRS 600 Dynamically Regenerated Suppressor (2 mm) (P/N 088667)
- Optional Thermo Scientific™ Dionex™ CRD 300 Carbonate Removal Device (2 mm) (P/N 064638)

Reagents and standards

- Deionized water (DI), Type 1 reagent grade, 18 MΩ·cm resistivity or better
- Thermo Scientific™ Dionex™ AS22 Eluent Concentrate (P/N 063965)
- Thermo Scientific™ Dionex™ Nitrite Standard 1,000 mg/L (P/N 303169)
- Thermo Scientific™ Dionex™ Chloride Standard 1,000 mg/L (P/N 037159)
- Thermo Scientific™ Dionex™ Sulfate Standard 1,000 mg/L (P/N 037160)
- Thermo Scientific™ Dionex™ Fluoride Standard 1,000 mg/L (P/N 037158)

- Thermo Scientific™ Dionex™ Phosphate Standard 1,000 mg/L (P/N 303172)
- Thermo Scientific™ Dionex™ Nitrate Standard 1,000 mg/L (P/N 056497)
- Fisher Chemical™ Sodium Bromide (P/N S255)
- J.T. Baker™ Sulfuric Acid (P/N 9681) for chemical regenerant

Instrument method

Parameter	Value	
Instrument	Dionex Inuvion IC system	
Columns	Dionex IonPac AS22 analytical column, 2 × 250 mm Dionex IonPac AG22 guard column, 2 × 50 mm	
Eluent	4.5 mM sodium carbonate and 1.4 mM sodium bicarbonate, made using Dionex AS22 eluent concentrate	
Flow rate	0.5 mL/min	
Column temp.	30 °C	
Inj. volume	5 µL full loop	
Run time	10 minutes	
Detection	Chemical suppression Suppressed conductivity with a Dionex ACRS 500 suppressor, chemically regenerated with 25 mM sulfuric acid at 1 mL/min delivered by regen pump.	Electrolytic suppression Suppressed conductivity with a Dionex ADRS 600 suppressor in constant current mode at 13 mA and recycling water mode. Dionex CRD 300 carbonate removal device in vacuum mode with VP pump.
Background conductance	<21 µS/cm	<1 µS/cm
System back-pressure	≈2,600 psi	≈2,400 psi

Standard preparation

To prepare 1,000 mg/mL bromide standard solution, 257.5 mg of sodium bromide was dissolved in 20.0 g of DI water and then further diluted 10-fold. Other anion standard solutions (1,000 mg/mL each) were purchased from vendors listed above.

A stock standards mixture was prepared by mixing each 1,000 mg/mL solution in equal parts. This stock standard mixture was then further diluted to be used for calibration. Eleven calibration standards were prepared in the following concentrations for each anion: 0.04, 0.09, 0.18, 0.36, 0.71, 1.43, 4.76, 14.29, 35.71, 47.62, and 71.43 mg/L.

Sample preparation

Water samples from various sources were filtered through a syringe filter (pore size: 0.45 µm, PES) and injected for analysis.

Results and discussion

Separation

Figure 1 shows the separation of seven anion standards using (i) a chemically regenerated suppressor and (ii) an electrolytically regenerated suppressor with an optional carbonate removal device (CRD). All seven peaks were well-resolved within 8 minutes in both cases. In chromatogram ii, the effectiveness of the CRD is showcased by reducing background conductivity, resulting in the minimizing of the initial water dip and increased peak sensitivity.² In this experiment, 30% improvement of the limit of detection (LOD) and the limit of quantitation (LOQ) for fluoride were observed with the setup using the CRD (Table 1). It can also aid in improving peak shape in water samples that are high in ionic interference.

Detection: i: Suppressed conductivity detection with a Dionex ACRS 500 chemically regenerated suppressor with 25 mM sulfuric acid as regenerant
ii: Suppressed conductivity detection with a Dionex ADRS 600 electrolytic suppressor in constant current mode and a Dionex CRD 300 carbonate removal device

Peaks: 1. Fluoride
2. Chloride
3. Nitrite
4. Bromide
5. Nitrate
6. Phosphate
7. Sulfate

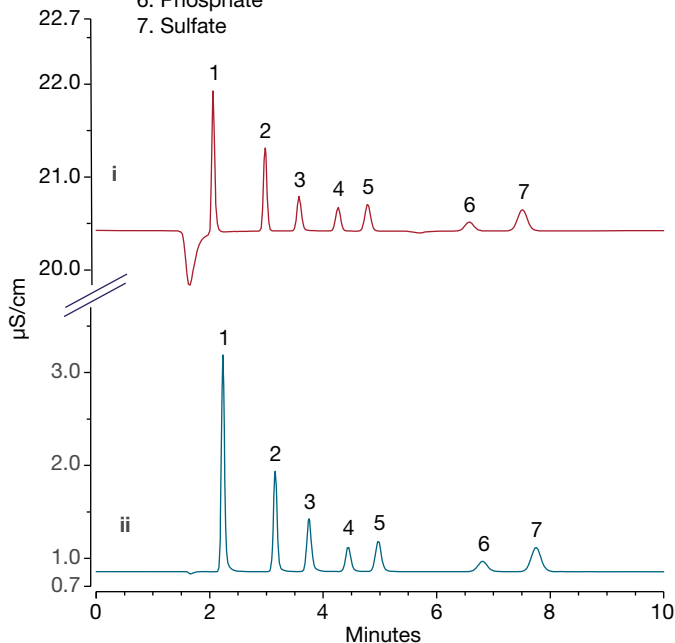


Figure 1. Seven anion standards in DI water with each anion at a concentration of 1 mg/L. (i) Suppressed conductivity detection with the Dionex ACRS 500 chemically regenerated suppressor. (ii) Suppressed conductivity detection with the Dionex ADRS 600 electrolytic suppressor, coupled with a CRD. The reduced background conductivity is due to the use of the CRD.

Without the CRD, the chromatograms on both settings will look similar as shown in Figure 2.

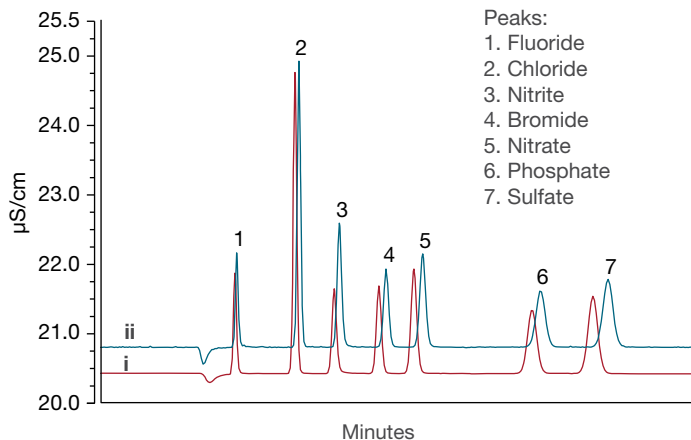


Figure 2. Example chromatograms of seven anions without the CRD.

Both setups show similar initial water dip and background noise. (i) Suppressed conductivity detection with the Dionex ACRS 500 chemically regenerated suppressor with 25 mM sulfuric acid as regenerant. (ii) Suppressed conductivity detection with the Dionex ADRS 600 electrolytic suppressor.

Calibration and estimated detection and quantitation limits

The retention time (RT) and calibration information for both setups showed similar effectiveness (Table 1). Relative standard error (RSE) was used as an evaluation method of calibration curves instead of traditional relative standard deviation (RSD). This is because RSE standardizes precision assessment across various scales and enhances calibration quality.³

LOD and LOQ were calculated following the International Council for Harmonisation (ICH) guidelines.⁴ The templates to perform these calculations directly in Chromeleon CDS are part of the Chromeleon CDS ICH-extension pack.

$$LOD = \frac{3.3 \sigma}{S} \quad LOQ = \frac{10 \sigma}{S}$$

where σ = the standard deviation of the response
 S = the slope of the calibration curve

Resolution

The Dionex IonPac AS22 column is designed for compliance monitoring of inorganic anions in accordance with U.S. EPA Methods 300.0 and 300.1. Figure 3 demonstrates the resolution of inorganic anions specified in the EPA methods.⁵

Table 1. Calibration information, LOD, and LOQ for anions using chemically suppressed conductivity detection with a Dionex ACRS 500 suppressor and electrolytically suppressed conductivity detection with a Dionex ADRS 600 suppressor and a CRD. Number of calibration levels = 11. Calibration standard range = 0.04–71.43 mg/mL. Calibration type = Quad, WithOffset, 1/A².

	Calibration						Limits			
	Chemical suppression			Electrolytical suppression			Chemical suppression		Electrolytical suppression	
	RT (min)	RSE (%)	R ²	RT (min)	RSE (%)	R ²	LOD (µg/L)	LOQ (µg/L)	LOD (µg/L)	LOQ (µg/L)
Fluoride	2.06	8.8	0.997	2.23	8.4	0.992	1.51	4.56	1.06	3.20
Chloride	2.98	9.2	0.998	3.15	9.0	0.989	0.99	3.01	0.82	2.50
Nitrite	3.57	7.7	0.999	3.75	8.3	0.990	1.36	4.12	0.76	2.30
Bromide	4.24	3.4	1.000	4.43	6.0	0.991	1.25	3.79	1.32	4.00
Nitrate	4.76	9.8	0.997	4.96	6.6	0.992	3.05	9.23	2.51	7.61
Phosphate	6.56	9.7	0.998	6.78	5.5	0.992	6.58	19.94	6.19	18.75
Sulfate	7.53	5.0	0.999	7.75	6.4	0.991	3.68	11.14	2.42	7.33

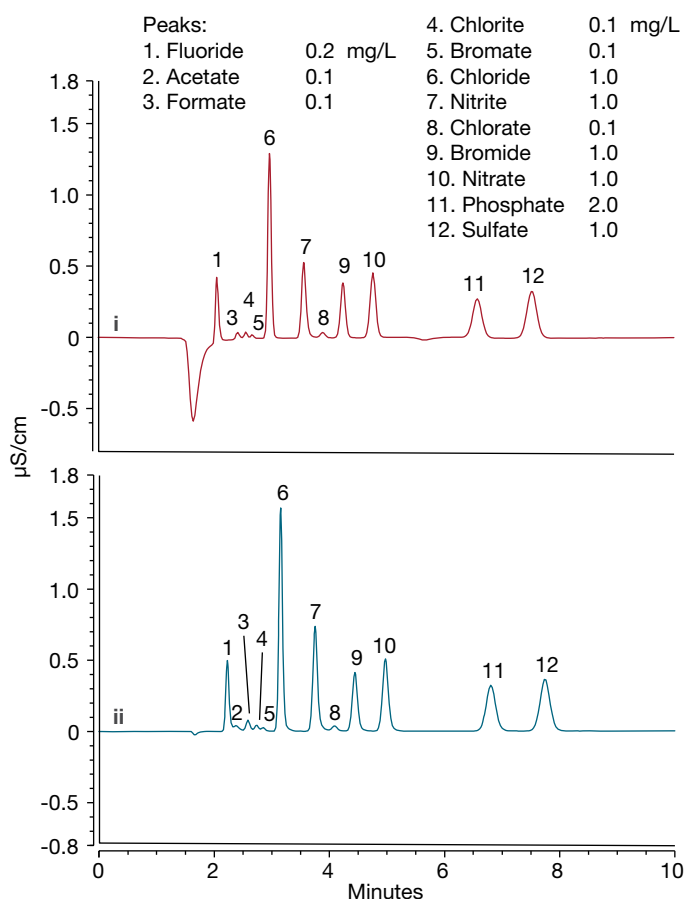


Figure 3. Resolution of common inorganic anions with both chemical suppression (i) and electrolytical suppression (ii)

Analysis of anions in matrices with high ionic strength

To demonstrate the resolution of anions in high ionic strength wastewater, a standard was prepared with 1,000 mg/L each chloride and sulfate to simulate wastewater matrix. Figure 4 shows the chromatograms of these standards using chemically and electrolytically suppressed conductivity detection. Recoveries of 78–117% were achieved for five common inorganic anions, demonstrating the effectiveness of the method for the analysis of wastewater.

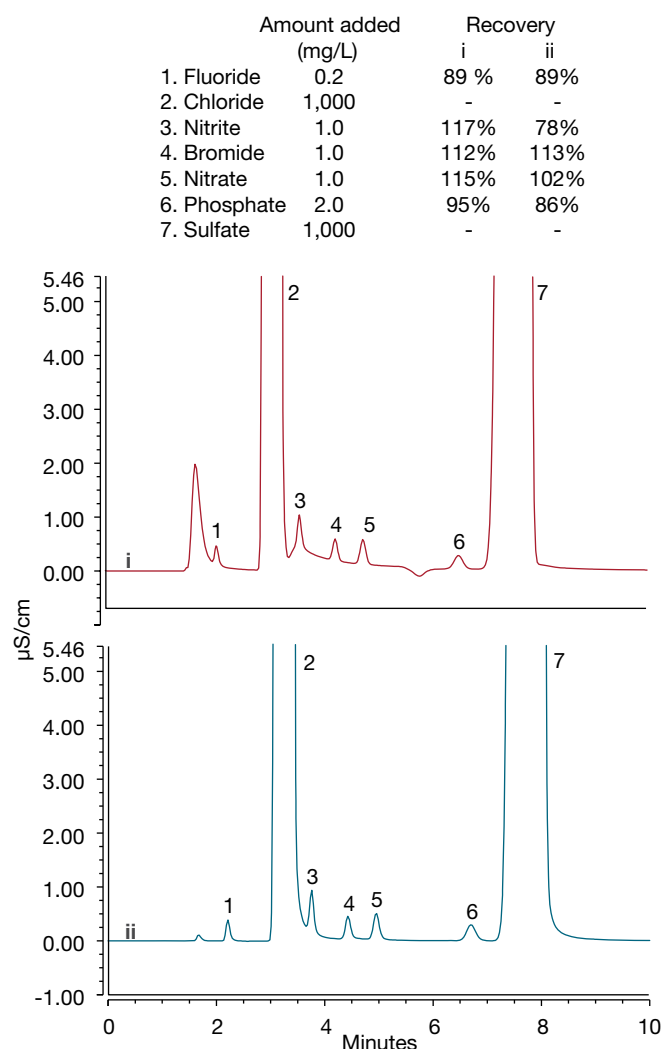


Figure 4. Resolution of anions in high ionic strength matrices. (i) Chemically suppressed conductivity detection with an ACRS suppressor. The nitrite peak was manually integrated due to poor baseline shape. (ii) Electrolytically suppressed conductivity detection with a CRD.

Robustness

To assess the robustness of the method, we evaluated changes in the retention time (RT) and peak area count of a check standard across multiple injections. For the chemical suppression setup, a total of 528 injections were performed. Similarly, for the electrolytic suppression setup, a total of 524 injections were conducted.

Both setups included a diverse range of water samples: 28 injections of drinking water, 180 injections of wastewater,

60 injections of pond water, and 20 injections of aquarium water. This comprehensive testing ensured the method's applicability across various water types.

The results demonstrated the stability of both suppression methods, as evidenced by the low RSD values presented in Table 2 and illustrated in Figure 5. These findings underscore the reliability and consistency of the method, making it a robust choice for anion analysis in different water matrices.

Table 2. RSD of RT and area count for 20 injections of check standard, injected between every 20–40 standard/sample blocks over 500 injections

	RT RSD (%)		Area RSD (%)	
	Chemical suppression	Electrolytical suppression	Chemical suppression	Electrolytical suppression
Fluoride	0.11	0.07	0.49	0.76
Chloride	0.06	0.09	0.31	0.48
Nitrite	0.11	0.15	1.29	0.96
Bromide	0.17	0.22	0.28	0.88
Nitrate	0.18	0.23	0.28	0.88
Phosphate	0.17	0.24	0.32	1.16
Sulfate	0.23	0.16	0.32	1.09

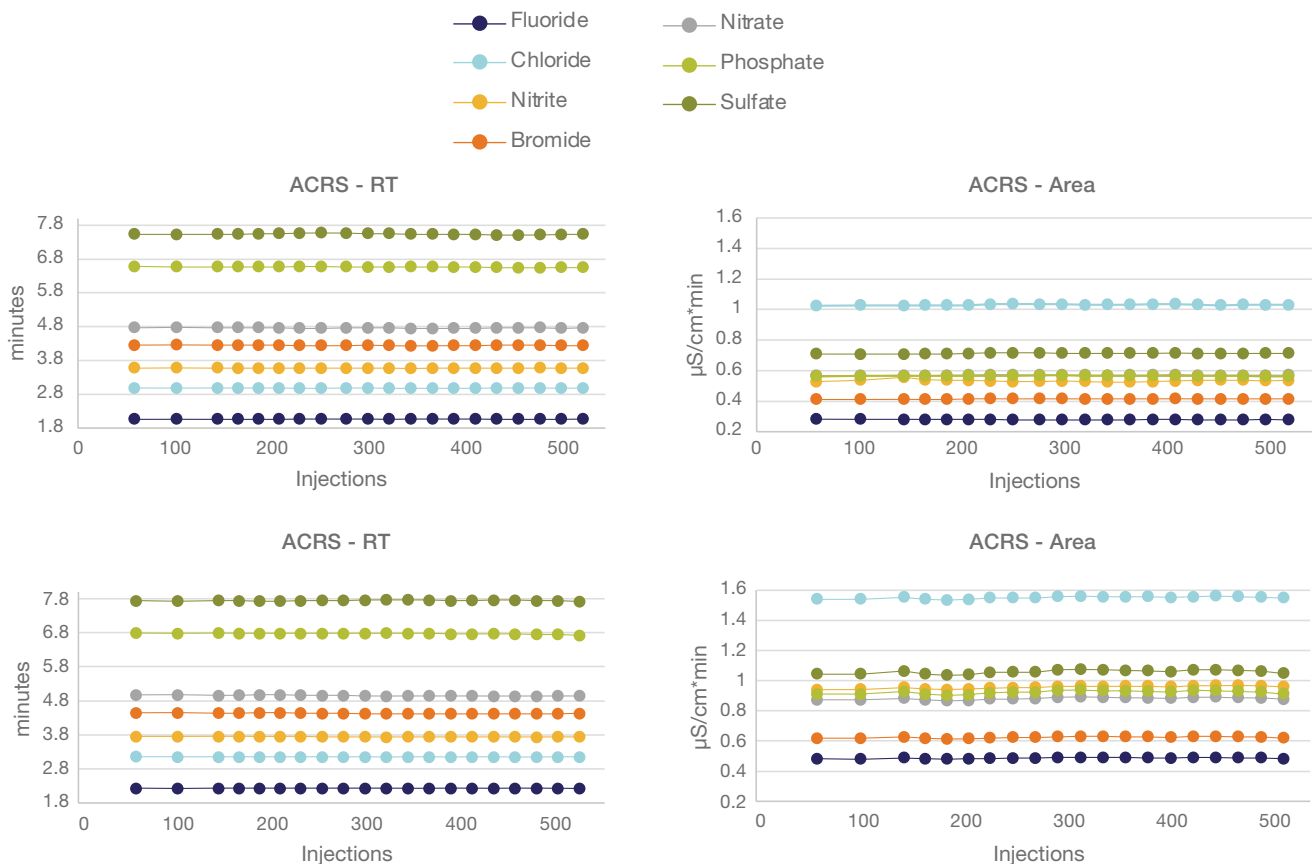


Figure 5. The change in RT and area count of check standard measured intermittently over 500 injections to show robustness of the method. N = 20, injected between standard/sample blocks.

Sample analyses

Various water samples were tested, and results are shown below (Figure 6, Tables 3a and 3b). Both chemical suppression

setup and electrolytical suppression show similar results, further validating the accuracy of both methods.

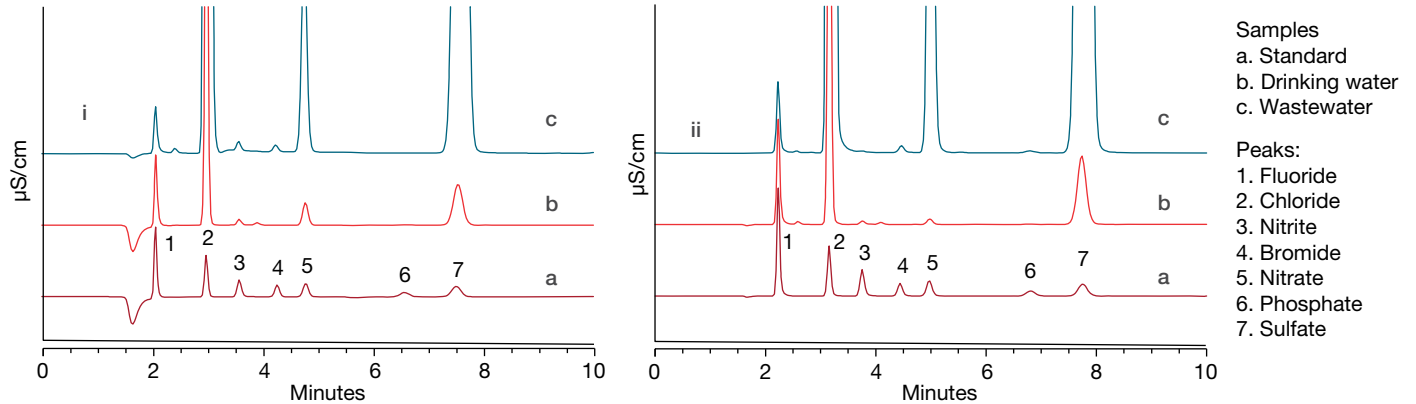


Figure 6. Comparison of water analysis: (i) chemical regeneration; (ii) electrolytical regeneration with CRD

Table 3a. Analysis of municipal drinking water (mg/L). ND = Not detected

	Location A		Location B		Location C		Location D	
	ACRS	ADRS	ACRS	ADRS	ACRS	ADRS	ACRS	ADRS
Fluoride	0.71	0.70	0.69	0.70	0.71	0.70	0.11	0.10
Chloride	6.34	6.79	5.66	6.29	5.88	6.50	58.31	56.98
Nitrite	0.24	0.11	0.01	0.01	ND	ND	ND	ND
Bromide	0.01	0.01	0.01	0.01	0.00	0.01	0.08	0.06
Nitrate	1.19	0.25	0.35	0.28	0.41	0.34	19.58	21.31
Phosphate	0.07	0.07	ND	ND	0.01	ND	0.13	0.10
Sulfate	2.69	3.37	1.53	1.39	1.87	1.73	61.98	59.33

Table 3b. Analysis of waste and other water (mg/L)

	Wastewater A		Wastewater B		Wastewater C		Pond		Aquarium	
	ACRS	ADRS	ACRS	ADRS	ACRS	ADRS	ACRS	ADRS	ACRS	ADRS
Fluoride	0.49	0.50	0.93	0.95	0.92	0.97	0.21	0.20	1.02	1.25
Chloride	145.09	140.62	72.60	70.10	72.37	70.19	34.00	34.34	127.94	131.57
Nitrite	0.38	0.03	0.02	0.02	ND	ND	ND	ND	0.06	0.03
Bromide	0.40	0.39	0.04	0.05	ND	0.05	0.11	0.10	0.12	0.10
Nitrate	10.48	26.21	0.01	0.02	ND	0.04	0.02	0.02	210.12	187.46
Phosphate	0.05	0.27	21.93	24.25	21.41	23.92	ND	ND	8.17	10.61
Sulfate	93.80	84.96	14.81	16.49	13.72	16.79	53.57	52.78	134.06	116.67

Lower liquid waste

A microbore column requires a lower flow rate than a standard bore 4 mm column while still delivering comparable resolution. Moreover, incorporating an electrolytic suppressor eliminates the need for a chemical regenerant. Table 4 presents an estimation

of the waste produced for both chemical regeneration and electrolytic regeneration setups, comparing the 2 mm microbore column and a standard bore 4 mm column. This calculation assumes continuous operation with a 3-minute interval between injections and considers a chemical regenerant flow rate that is twice the analytical flow rate, if applied.

Table 4. Estimated amount of liquid waste produced for a 4 mm IC column and 2 mm column

	Flow rate (mL/min)	Run time (min)	Number of injections (per day)	Liquid waste produced after 10 days (L)	
				ACRS	ADRS
4 mm ID	1.2	14	85	51.8	17.3
2 mm ID	0.5	10	111	21.6	7.2

The synergy of a reduced flow rate and shorter run times allows the microbore column to produce less than half the volume of liquid waste compared to the standard bore column. Additionally, the use of electrolytical suppression in recycling mode, which eliminates the need for chemical regenerant, further drastically reduces waste production.

The results underscore the environmental advantages of the microbore column, making it a compelling choice for laboratories aiming to minimize their ecological footprint while maintaining high analytical performance.

Lower flow rates and shorter run times lead to waste reduction. The use of an electrolytic suppressor in recycling water mode further reduces waste.

Conclusion

This application note showcases a fast and efficient analysis of common anions while significantly reducing the volume of liquid waste generated with a microbore column and electrolytic suppression, as compared to a standard bore column and a chemically regenerated suppressor. The adoption of microbore columns plays a pivotal role in waste reduction by utilizing a lower

flow rate. Both chemical and electrolytic suppression techniques yield comparable results; however, electrolytic suppression offers the added advantage of minimizing the need for manual preparation of chemical regenerants, thereby further decreasing liquid waste as well as removing a need to handle dangerous chemicals. This setup not only proves to be robust and reliable but also exemplifies a more environmentally sustainable approach to anion analysis.

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