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Determination of trace level ions by high-volume direct-injection ion chromatography

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Abstract

A high-volume direct-injection method was developed for the purpose of trace level determinations (low to sub-μg/l) of anions and cations by ion chromatography. The chromatographic signal was enhanced by increasing the sample volume up to 1300 μl with no significant loss in peak efficiency. The following parameters were optimized for minimizing noise: eluent flow, background conductance, suppressor chemistry, conductivity temperature and data filtering. Total analysis times were less than 30 min and the method detection limits for most ions ranged from 10 to 400 ng/l (ppt).

Keywords: Ion chromatography; Trace-level anions/cations; Chloride; Sodium

1. Introduction

Ion chromatography (IC) is regarded as a versatile analytical technique for separating and quantifying ions. IC was first developed by Small and coworkers in 1975 [1]. With advancements in column, separation, detection and data analysis technology, IC analysis has matured to a rugged, sensitive and reliable analysis technique for a wide variety of ionic species.

There has been considerable interest in the determination of ions at trace levels by IC. For this investigation we will define "trace" as determinations at or below 1 μg/l (ppb) levels. For example, the Electric Power Research Institute has established IC as the analytical technique for determining sodium, chloride and sulfate down to 0.25 μg/l in power plant waters [2]. For high-purity water used in semiconductor processing, the Semiconductor Equipment and Materials International (SEMI) recomends the use of IC for tracking trace ionic contaminants from 0.025 to 0.5 μg/l [3].

To determine ions at mid μg/l to mg/l (ppb to ppm) levels with IC, a sample size of 10 to 50 μl is sufficient. To determine ions at lower levels, then a preconcentration or trace enrichment technique has typically been utilized [4,5]. With this method, the analytes of interest are preconcentrated on another column in order to "strip" ions from a measured sample volume. This process concentrates the desired species resulting in lower detection limits.

However, preconcentration has several disadvantages. Compared with a direct method, additional hardware is required. A concentrator column is used to preconcentrate the ions of interest. A sample pump is needed for loading sample. An additional valve is often required for switching the concentrator column in and out-of line with the analytical column.

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Extra time is required for the preconcentration step. Also, analyte loading efficiency can be compromised when additives are present. This occurs because the matrix acts as an eluent to elute ions that have been retained on the concentrator column.

It was of interest to explore the development of a high-volume direct-injection IC method that would facilitate trace ion determinations without a separate preconcentration step. This would represent a significantly simpler and more reliable means of trace analysis. This paper describes the evaluation of on-column preconcentration for enhancing sensitivity and enabling trace ion determination in high-purity water.

2. Experimental

2.1. Chromatographic system

All chromatography was performed on a Dionex (Sunnyvale, CA, USA) DX-500 ion chromatograph. The system consisted of a gradient pump (GP40), a liquid chromatography module (LC20) and a conductivity detector (CD20). The CD20 utilized a Dionex DS3 thermally controlled conductivity cell. A PC equipped with Dionex PeakNet chromatography software was utilized for data acquisition, instrument control and data smoothing.

For sample loading, a Rheodyne (Cotati, CA, USA) Model 9126-038 injection valve configured for rear loading was utilized. Two methods of sample loading were employed to minimize the possibility of contaminating the sample by handling. The first method utilized a pressurizable reservoir chamber (Dionex) pressurized with air at 5 p.s.i. (34 kPa) as shown in Fig. 1. The low pressure slider valve (Dionex) was used to regulate the flow of sample into the loop. The second method simply used a disposable syringe at the waste port of the injection valve to draw sample into the loop from the sample container.

Sample loops were made from PEEK (polyether-ether ketone) tubing with either: 0.020 in. I.D.× 0.062 in. O.D. (0.51 mm I.D.×1.57 mm O.D.) or 0.030 in. I.D.×0.062 in. O.D. (0.76 mm I.D.×1.57 mm O.D.) Loop volumes were verified by an analytical balance capable of accurately weighing to the nearest 0.0001 g. This was accomplished by using the mass difference when loops were filled with and without deionized water.

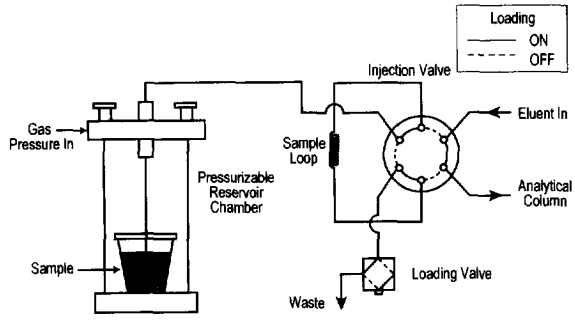

Fig. 1. IC system configuration for direct-injection sample loading.

All columns used in this study were manufactured by Dionex. For anion separations an IonPac AS10 (2×250 mm and 4×250 mm), IonPac AG11 (2×50 mm and 4×50 mm) and IonPac AS11 (2×250 mm) were utilized. The IonPac AS10 was used for isocratic separations of common inorganic ions, acetate, formate and oxalate. The IonPac AS11 was used with a sodium hydroxide gradient (0.5 m*M* to 26 m*M* NaOH) to separate inorganic anions and organic acids. For the AS11 separation, an ATC 2 mm (4×35 mm) was utilized to minimize the baseline shift of the gradient. Table 1 summarizes the anion analytical conditions.

A mixed-bed trap column was used as an on-line trap to obtain a high-purity water blank low in trace anions. To make this column, we packed nuclear grade Bio-Rex RG 501-X8 (Bio-Rad, Richmond, CA, USA) mixed-bed resin into a 4×50 mm column body.

For cation separations, an IonPac CS 12A (2×250 mm) was utilized. This column permits the isocratic separation of monovalent and divalent cations using a sulfuric acid eluent. Table 2 summarizes the cation chromatographic conditions.

Suppressed conductivity detection was used. An anion self regenerating suppressor (ASRS) and cation self regenerating suppressor (CSRS) from Dionex were utilized for the anion and cation separations respectively. Anion suppressors were operated in the external water mode, cation suppressors in the recycle mode [6]. Deionized water with a

Table 1
Anion chromatographic conditions

IonPac AS10		
Analytical column	AS10 (2×250 mm)	
Trap column	ATC (2 mm)	
Eluent	85 m*M* sodium hydroxide	
Eluent flow-rate	0.25 ml/min	
Injection volume	900 μL	
Detection	Suppressed conductivity	
Suppressor	Anion self regenerating suppressor (ASRS), External water mode	
ASRS current	500 mA	
IonPac AS11	2 mm	4 mm
Guard column	AG11 (2×50 mm)	AG11(4×50 mm)
Analytical column	AS11 (2×250 mm)	AS11 (4×250 mm)
Trap column	ATC (2 mm)	ATC (4 mm)
Eluent	Sodium hydroxide gradient 0.5 m*M* to 2.5 min rising to 5.0 m*M* at 6 min and to 26 m*M* at 20 min	(same as 2 mm)
Eluent flow-rate	0.5 ml/min	2.0 ml/min
Injection volume	750 μL	500 μL
Detection	Suppressed conductivity	(same as 2 mm)
Suppressor	ASRS, 2 mm External water mode	ASRS, 4 mm
ASRS current	300 mA	(same as 2 mm)

specific resistance of 17.8 MΩ cm or greater was delivered to the ASRS by means of an air-pressurized plastic 4-l vessel. A flow-rate between 5 and 7 ml/min was achieved by adjusting air pressure to the vessel with up to 25 p.s.i. (172 kPa).

2.2. Chemicals

High purity deionized water (DI H_2O) with a specific resistance of 17.8 MΩ cm or greater was used for preparing rinse solution, eluent and standards. It, was supplied by either a Barnstead (Dubuque, IA, USA) or Labconco (Kansas City, MO, USA) point-of-use high-purity water system. This DI H_2O had minimal levels of ionic impurities (<0.1 μg/l), organics, microorganisms and particulate matter (larger than 0.2 μm).

Reagent grade chemicals and deionized water were used for standard and eluent preparation. Sodium hydroxide, 50% (w/w) from Fisher (Pittsburgh, PA, USA) was used to prepare the anion eluents.

Table 2
Cation chromatographic conditions

Analytical column	CS12A (2×250 mm)
Eluent	11 m*M* sulfuric acid
Eluent flow-rate	0.25 ml/min
Injection volume	1000 μl
Detection	Suppressed conductivity
Suppressor	Cation self regenerating suppressor (CSRS), 2 mm Recycle mode
CSRS current	100 mA

Trace metal grade sulfuric acid (Baker, Phillipsburg, NJ, USA) was used to prepare the cation eluent.

Anion and cation standards (1000 mg/l) were prepared from reagent grade salts. Working standards were prepared by further diluting the 1000-mg/l standards to the range expected for the ions of interest. Polyethylene containers presoaked with deionized water were used to store samples and standards.

The amine-treated water matrix was made with ethanolamine (Aldrich, Milwaukee, WI, USA), ultra-high-purity grade boric acid (Alfa AESAR, Ward Hill, MA, USA) and ammonium hydroxide (Baker) diluted with high-purity deionized water.

Special care was taken to minimize contamination. Polyethylene containers were soaked for at least 24 h with DI H_2O and rinsed several times prior to use. Disposable gloves were worn at all times when handling apparatus that contacted standards or samples.

3. Results and discussion

3.1. Factors affecting trace analysis

Experimental factors that affect signal-to-noise were optimized for maximum sensitivity, accuracy, and reproducibility. Controlling these factors was important because the magnitude of the analyte signal approaches the magnitude of the noise when analyzing at trace levels. Fig. 2 illustrates this, the top chromatogram has a signal-to-noise ratio (S/N) of 10, the bottom has a S/N of 30. Signals become more difficult to quantify as S/N decreases [7].

Factors that affect the signal include the mass, concentration and form of the analyte. It was our goal that the analyte mass injected be as large as possible to yield the maximum signal possible. However this should not be done at the expense of excessive band broadening or coelution of neighboring peaks [8]. The use of eluent suppression resulted in an increase in analyte conductivity because the analyte ions were converted to the acid or base form [9].

Factors that contribute to noise include each component of the analysis system: the pump, suppressor and conductivity cell. Our experience has

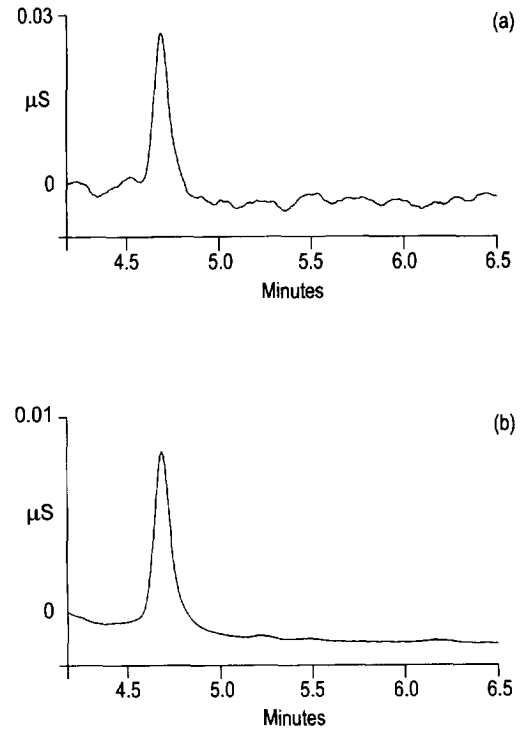

Fig. 2. Effect of concentration on signal-to-noise ratio for an IC peak. (a) $S/N=10$ (0.03 μg/l formate); (b) $S/N=30$ (0.11 μg/l formate). Column: IonPac AS11 (2×250 mm). Guard column: IonPac AG11 (2×50 mm). Detection: conductivity. Suppression: ASRS, external water mode. Eluent: 0.5 m*M* sodium hydroxide. Eluent flow-rate: 0.50 ml/min.

shown that a liquid chromatography pump can contribute significant noise (>10 nS peak-to-peak noise for 1 min) especially in gradient separations. The pump used in this study uses artificial intelligence algorithms that minimizes pump pulsations caused by changing eluent conditions [10]. Use of chemical suppression, reduces the background conductance of the eluent and proportionately reduces baseline noise and drift. [9] By selecting the SRS current settings best matched to a given eluent concentration and flow-rate, the minimum baseline noise was achieved for each method. A representative example is shown in Fig. 3.

Temperature has a major effect on the conductivity of a solution. Experimentally, conductivity has been found to rise about 2% per °C [11]. During the course of an IC analysis ambient temperature fluctuations will result in noticeable oscillations in the

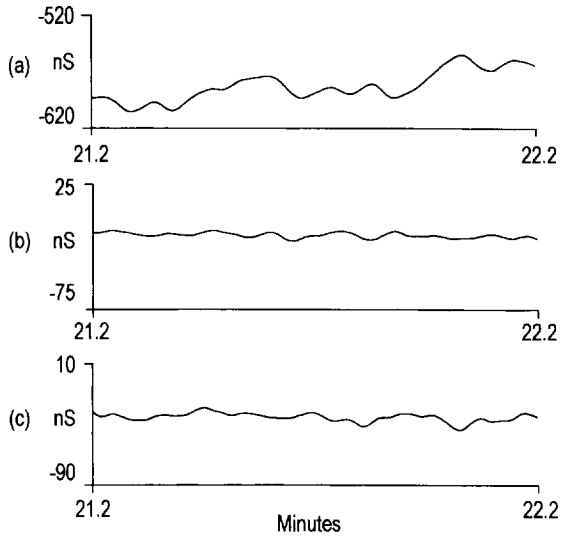

Fig. 3. Effect of ASRS current setting on noise. Column: IonPac AS10 (2×250 mm). Detection: conductivity. Suppression: ASRS, external water mode. Eluent: 85 m*M* sodium hydroxide, isocratic. Eluent flow-rate: 0.25 ml/min. (a) 50 mA, noise 33 nS; (b) 100 mA, noise 8.2 nS; (c) 300 mA, noise 17 nS.

conductivity baseline. The stabilized cell used in this work allowed us to measure conductivity at a constant operating temperature. This minimized fluctuations in cell temperature which improved detection at trace levels.

All columns used in this study were in the microbore (2 mm I.D.) format, except that used in data smoothing. This column format has several advantages over the standard 4 mm [12]. A smaller sample volume (1/4) is required which results in more convenient and faster loop loading. Also 1/4 of the eluent is required because the flow can be reduced. This facilitates round-the clock operation with less frequent eluent changes and thus results in more reproducible chromatography and background conductivity. Overall the system has improved stability and reliability thus requiring less operator intervention.

3.2. Anion method performance

With instrument components such as the pump, suppressor and conductivity cell optimized for minimal noise, trace anion determination with the use of an isocratic AS10 separation was evaluated. Sample

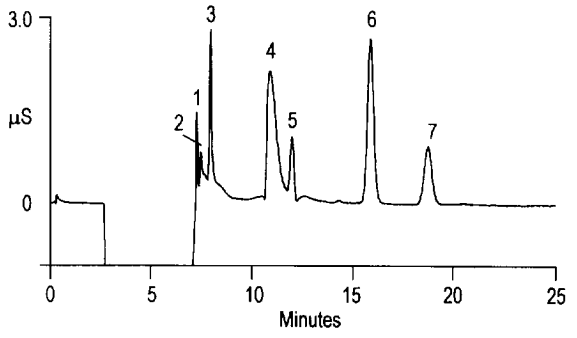

Fig. 4. Trace anions by direct injection with 900-μl sample size. Anion standard solution. Peaks: 1=fluoride (2 μg/l); 2=acetate (4 μg/l); 3=formate (4 μg/l); 4=carbonate; 5=chloride (3 μg/l); 6=sulfate (20 μg/l); 7=oxalate (15 μg/l). Sample volume: 900 μl; Column: IonPac AS10 (2×250 mm). Detection: conductivity. Suppression: ASRS, external water mode. Eluent: 85 m*M* sodium hydroxide, isocratic. Eluent flow-rate: 0.25 ml/min.

volume was varied by changing the size of the injection loop from 10 to 900 μl. Fig. 4 shows the result of the 900-μl injection. It can be seen that all peaks are well resolved with early eluting peaks out of the system void. Table 3 shows a significant improvement in detection limits (calculated using three times the noise) as the sample volume was increased.

It was also of interest to apply the high-volume direct-injection analysis approach to a gradient anion separation. The IonPac AS11 column was selected because of its high resolving power for inorganic anions and organic acids. Sample volume was varied to determine the optimum operating conditions as before. Fig. 5 shows that no significant loss in column efficiency was detected as sample volume was varied from 25 to 750 μl. It is also worth noting

Table 3
Detection limits[a] (μg/l) as a function of sample volume AS10, 2 mm

Analyte	Sample volume (μl)			
	10	100	300	900
Fluoride	3.2	0.38	0.12	0.038
Acetate	24	2.6	1.2	0.27
Formate	11	1.8	0.68	0.30
Chloride	12	1.1	0.42	0.13
Sulfate	9.1	0.83	0.36	0.13
Oxalate	20	2.6	1.1	0.35

[a] 3×noise.

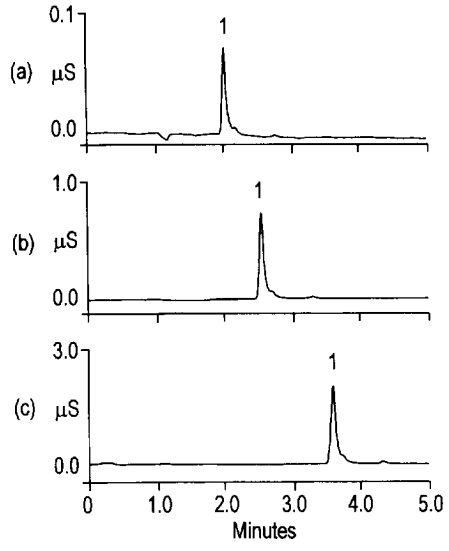

Fig. 5. Sample loop volume versus retention time: (a) 25 μl; (b) 250 μl; (c) 750 μl. Sample: 10 μg/l fluoride. Peak 1=fluoride. Analytical column: IonPac AS11 (2×250 mm). Guard column: IonPac AG11 (2×50 mm). Detection: conductivity. Suppression: ASRS, external water mode. Eluent: 0.5 m*M* sodium hydroxide. Eluent flow-rate: 0.50 ml/min.

the absence of a large system void that obscures early eluting analytes. The baseline disturbance from the system void was minimized because the large aqueous sample was introduced into a mobile phase of low conductivity background (≤1 μS for 0.5 m*M* sodium hydroxide).

Fig. 6 shows the separation of ten anions at low to sub μg/l using a 750-μl sample. Detection limits are comparable to those shown in Table 3 for the 900-μl injection on the AS10 separation. A blank was prepared by passing high-purity DI H_2O through a mixed-bed ion-exchange resin. Fig. 7 shows the blank analysis with trace quantities of fluoride, acetate, and formate detected at less than 10 ng/l.

An ATC (2 mm) was utilized to help minimize artifact peaks and to keep the baseline shift of the gradient to less than 1 μS. This shift is caused by the elution of retained anionic contaminants as the ionic concentration of the eluent is increased. The ATC column contains a high capacity anion-exchange resin in the hydroxide form which is used to trap these ionic contaminants. The ATC was initially prepared for use by flushing (2 ml/min) with 200 ml of 200 m*M* sodium hydroxide followed by the

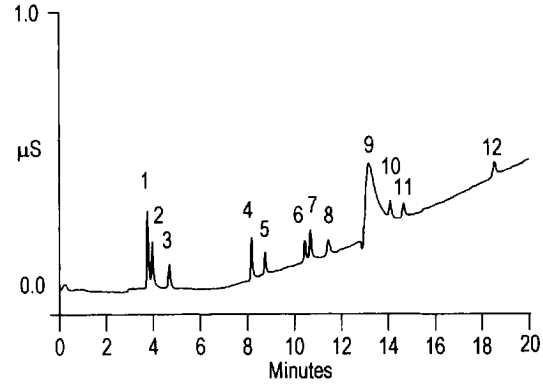

Fig. 6. Sub μg/l anion standard by direct injection. Peaks: 1=fluoride (1.4 μg/l); 2=acetate (3.0 μg/l); 3=formate (0.88 μg/l); 4=chloride (1.2 μg/l); 5=nitrite (0.71 μg/l); 6=bromide (1.6 μg/l); 7=nitrate (1.8 μg/l); 8=unidentified; 9=carbonate; 10=sulface (0.81 μg/l); 11=oxalate (1.3 μg/l); 12=phosphate (3.2 mg/l). Sample volume: 750 μl. Column: IonPac AS11 (2×250 mm). Guard column: IonPac AG11 (2×50 mm). Detection: conductivity. Suppression: ASRS, external water mode. Gradient conditions: 0.5 m*M* until 2.5 min rising to 5.0 m*M* at 6.0 min and to 26 m*M* at 20 min. Eluent flow-rate: 0.50 ml/min.

highest eluent used in the gradient program at the same flow-rate. The ATC was periodically regenerated using this procedure.

This method is also applicable to power plant high-purity waters containing corrosion inhibitors. A 750-μl sample of 8 mg/l ethanolamine, 8 mg/l boric acid and 300 μg/l ammonium hydroxide was analyzed by this method. Fig. 8 shows the separation of

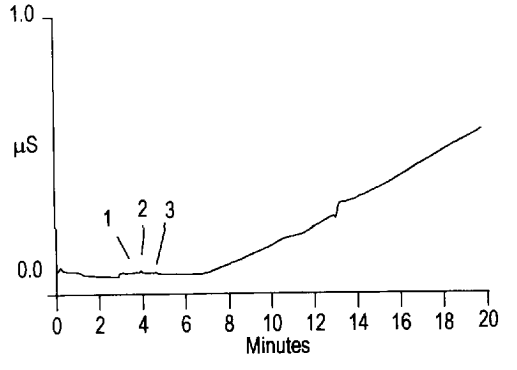

Fig. 7. High purity water blank by direct injection. Peaks: 1=fluoride (<10 ng/l); 2=acetate (<10 ng/l); 3=formate (<10 ng/l). Chromatographic conditions as in Fig. 5. Sample preparation: deionized water passed through a mixed-bed ion-exchange resin, then directly injected.

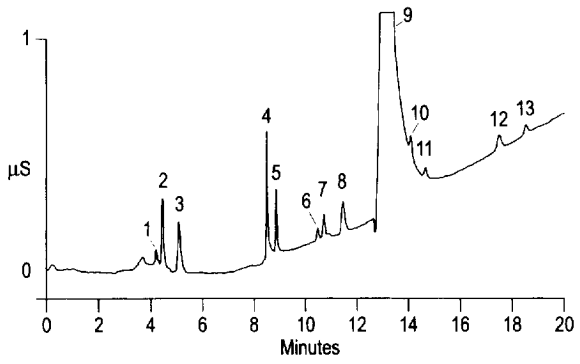

Fig. 8. Spiked sample of 8 mg/l ethanolamine, 8 mg/l boric acid and 0.3 mg/l ammonium hydroxide. Peaks: 1=fluoride (0.29 µg/l); 2=acetate (3.9 µg/l); 3=formate (2.1 µg/l); 4=chlroide (2.8 µg/l); 5=nitrite (1.8 µg/l); 6=bromide (0.97 µg/l); 7=nitrate (1.2 µg/l); 8=unidentified; 9=carbonate; 10=sulfate (0.63 µg/l); 11=oxalate (0.76 µg/l); 12=unidentified; 13=phosphate (1.6 µg/l). Chromatographic conditions as in Fig. 5.

a spiked standard in this matrix with no significant loss of peak efficiency or retention time when compared to the standard in water (Fig. 6). Precision was acceptable for seven repeat injections, with R.S.D.s at less than 10% for the ten anions of interest, see Table 4.

To determine linearity of the method for anions in the ethanolamine matrix, four anions (chloride, sulfate, phosphate and bromide) were spiked at 10 µg/l. Sample size was varied by using three injection loops: 25 µl, 250 µl and 750 µl. Table 5 shows the linear response of peak area with sample volume. This demonstrates that ions are quantitatively retained by this method, even in amine treated matrices. This represents a significant improvement

Table 4
Precision for spike sample of 8 mg/l ethanolamine, 8 mg/l boric acid and 0.3 mg/l ammonium hydroxide for $n=7$

Anion	Concentration (µg/l)	R.S.D. (%)
Fluoride	0.31	6.2
Acetate	4.04	2.0
Formate	2.17	2.5
Chloride	2.90	1.8
Nitrite	2.09	8.1
Bromide	1.02	7.5
Nitrate	1.29	6.8
Sulfate	0.58	5.1
Oxalate	0.65	8.8
Phosphate	1.89	6.9

Table 5
Calibration data for spiked sample of 8 mg/l ethanolamine, 8 mg/l boric acid and 0.3 mg/l ammonium hydroxide

Anion	Calibration curve
Chloride	$y=0.0078x+7.6$ ($R^2=1.0000$)
Bromide	$y=0.027x-4.3$ ($R^2=0.9994$)
Sulfate	$y=0.018x-2.3$ ($R^2=1.0000$)
Phosphate	$y=0.029x-8.6$ ($R^2=0.9999$)

y=peak area; x=sample loop volume.
R^2=coefficient of determination.

over the problem experienced with the variable loading efficiency of the preconcentration in amine-treated matrices [13].

3.3. Cation method performance

The feasibility of the high-volume direct-injection method was evaluated for cations as well. The IonPac CS12A was selected because it could provide a fast separation of monovalent and divalent cations with an isocratic sulfuric acid eluent. The effect on detection limits when increasing sample size is illustrated in Fig. 9. Even at a sample volume of 1300 µl, minimal band broadening was observed. Detection limits determined at $S/N=3$ show a significant improvement in sensitivity, see Table 6.

3.4. Data smoothing

It was of interest to explore the benefits of data filtering for reducing the noise of chromatographs at

Table 6
Detection limits[a] (µg/l) as a function of sample volume for the CS12A, 2 mm column

Analyte	Sample volume (µl)	
	25	1000
Lithium	0.31	0.0071
Sodium	0.880	0.020
Ammonium	0.92	0.021
Potassium	1.9	0.042
Magnesium	1.4	0.031
Calcium	2.5	0.052

[a] 3×noise.

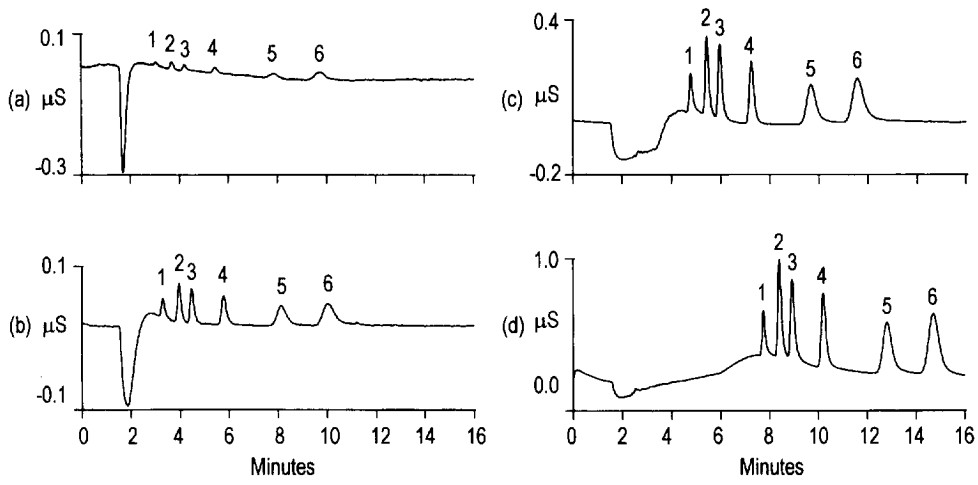

Fig. 9. Effect of sample loop size for cation separation of a standard mixture. Peaks: 1=lithium (0.38 µg/l); 2=sodium (1.5 µg/l); 3=ammonium (1.9 µg/l); 4=potassium (3.8 µg/l); 5=magnesium (1.9 µg/l); 6=calcium (3.8 µg/l). Sample volume: (a) 25 µl, (b) 100 µl, (c) 500 µl, (d) 1300 µl. Column: IonPac CS12A (2×250 mm). Detection: conductivity. Suppression: CSRS, recycle mode. Eluent: 11 m*M* sulfuric acid, isocratic. Eluent flow-rate: 0.25 ml/min.

trace levels. A least squares polynomial filtering capability in the chromatography software, introduced by Savitzky and Golay [14], was used post-run. The goal was to minimize noise without significantly degrading the analytical signal. The software allowed selection of two parameters: number of points (5–25) and number of iterations (1–99). A representative chromatogram subjected to the smoothing algorithm is shown in Fig. 10. A three-fold decrease in noise was realized with no more than 2% change in peak area. The parameters selected were (15) points with (10) iterations. Data that have been smoothed facilitates less ambiguous decisions as to where integration should start and end.

4. Conclusions

The methods described herein exhibit increased sensitivity and greater reliability than methods using conventional preconcentration. Lower detection limits were achieved by increasing sample size with no significant loss in peak efficiency nor in peak resolution. Trace levels (low to sub µg/l) were determined without the added complexity of a concentrator column or loading pump and valve. This method has also shown application to the determination of trace anions in amine treated waters. Data smoothing algorithms showed promise as a means for reducing noise and warrant further exploration.

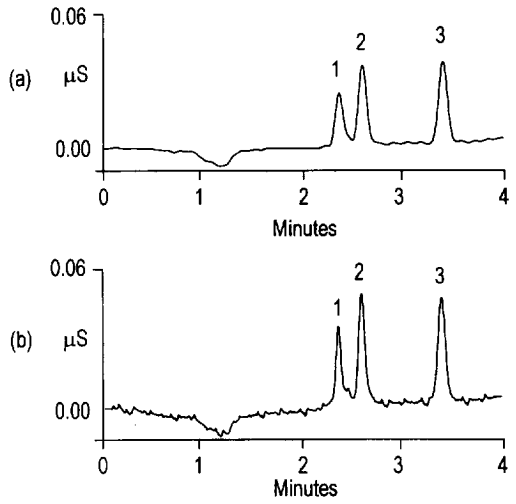

Fig. 10. Sub µg/l anion standard: (a) after smoothing and (b) without smoothing. Peaks: 1=fluoride (1.0 µg/l); 2=acetate (0.5 µg/l); 3=formate (1.0 µg/l). Sample volume: 500 µl. Column: IonPac AS11 (4×250 mm). Guard column: IonPac AG11 (4×50 mm). Detection: conductivity. Suppression: ASRS, external water mode. Gradient conditions: 0.5 m*M*. Eluent flow-rate: 2.0 ml/min. Details of smoothing algorithm in text.

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