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Studies on system performance and sensitivity in ion chromatography

P.E. Jackson^{a,*}, J.P. Romano^b, B.J. Wildman^b

^a*Waters Australia Pty. Ltd., Private Bag 18, Lane Cove, N.S.W. 2066, Australia*

^b*Waters Corporation, 34 Maple Street, Milford, MA 01757, USA*

Abstract

Improvements in HPLC instrumentation, suppressor technology and ion-exchange columns have occurred over the past several years to the point where an ion chromatograph can now be configured for anion analysis using a considerable variety of hardware, suppressor and column combinations. A number of parameters, including hardware configuration, effect of temperature, column type and suppressor device, were studied with a view toward optimizing the performance of an ion chromatographic (IC) system. It was found that dual-piston, reciprocating pumps used with low-pressure pulse dampeners significantly reduced baseline noise for both suppressed and non-suppressed conductivity detector combinations, while column temperature control proved essential in order to achieve routine sub-ppb detectability in non-suppressed IC. In general, the use of suppressed IC resulted in lower detection limits than non-suppressed IC when using the same columns and hardware. Of the columns studied, the methacrylate-based HR column was found to give the best overall separation selectivity when using a carbonate–bicarbonate eluent and suppressed conductivity detection. The majority of column and suppressor combinations evaluated gave acceptable performance, although some gave less than satisfactory results. Also, some combinations resulted in lower than expected analytical results, particularly for chloride, when quantitated using single-point calibration. In addition to the use of commercially available suppressor devices, there is also a large number of high-capacity cation exchangers which can be used as suppressors and these columns, in some instances, may offer equivalent (or superior) performance compared to the commercial devices.

1. Introduction

Ion chromatography (IC) is now the preferred (and regulatory approved) methodology for the determinations of anions in aqueous samples [1]. While the original scope of IC was limited to the determination of inorganic (and organic) anions and cations using an ion-exchange separation with conductivity detection [2], the growth of IC has seen the technique employed with a much wider range of separation and detection methods

[3]. Improvements in chromatographic hardware, column and suppressor technology have increased the range of solutes which can be analyzed, and also lowered the levels at which they can be detected.

Despite its widespread use, by far the most significant application of IC is the routine determination of the common inorganic anions, e.g. fluoride, chloride, nitrite, bromide, nitrate, phosphate and sulfate, in fresh water and wastewater samples [3]. A number of recent developments, including the expiration of the original packed-bed suppressor patent [4], has allowed

* Corresponding author.

further possibilities for anion analysis, in terms of hardware, column and suppressor combinations. The objective of this paper was to evaluate a number of possible combinations in order to determine an optimal IC system configuration. Parameters investigated include hardware configuration, the effect of temperature, column type and suppressor device. Results presented include sample quantitation, linearity, peak-area repeatability, efficiency, baseline noise data and detection limits for a variety of column and suppressor combinations.

2. Experimental

2.1. Instrumentation

The ion chromatograph consisted of Waters (Milford, MA, USA) 600 solvent delivery system, 717+ autosampler, 431 conductivity detector and a Millennium 2010 chromatography management system. Data were collected at 1 point/s. Three analytical columns were used: a Waters IC Pak Anion HR (75 × 4.6 mm I.D.), a Sarasep (Alltech, Sydney, Australia) AN 300 (100 × 7.8 mm I.D.) and a Dionex (Sunnyvale, CA, USA) AS4A-SC (250 × 4.0 mm I.D.). The Waters column was used with a borate–gluconate eluent at a flow-rate of 1.0 ml/min and also with an eluent of 1.2 mM bicarbonate–1.2 mM carbonate at 1.0 ml/min. Both the AN 300 and Dionex columns were used with an eluent of 1.7 mM bicarbonate–1.8 mM carbonate at 2.0 ml/min. The borate–gluconate eluent consisted of 1.6 mM sodium tetraborate, 7.3 mM boric acid, 1.6 mM sodium gluconate, 5 g/l glycerin, 120 ml/l acetonitrile and 20 ml/l *n*-butanol at pH 8.5. Two commercially available suppressor devices were used: an Alltech (Sydney, Australia) Model 335 solid-phase chemical suppressor (SPCS) and a Dionex anion micromembrane suppressor (AMMS). A regenerant of 25 mM sulfuric acid at 3.0 ml/min was used with the Dionex AMMS [5]. Two high-capacity cation-exchange columns were also used as suppressor devices: a Waters IC Pak C Cation-Guard (50 ×

4.6 mm I.D.) and Waters Fast Fruit Juice column (150 × 7.8 mm I.D.).

2.2. Reagents and procedures

Millipore (Bedford, MA, USA) Milli-Q 18-M Ω water was used for all eluent, sample and standard preparation. Sodium tetraborate, sodium carbonate, sodium bicarbonate, boric acid (all analytical-reagent grade) and glycerin (laboratory-reagent grade) were obtained from Ajax (Sydney, Australia), as were the analytical-reagent grade sodium salts used for the preparation of the anion standards. HPLC grade acetonitrile and *n*-butanol were also obtained from Ajax. Sodium gluconate (laboratory-reagent grade) was obtained from Fluka (Buchs, Switzerland). Eluents were prepared daily, filtered through a Millipore 0.45- μ m HV filter and degassed in an ultrasonic bath before use. High- and low-level anion standard mixtures were prepared containing fluoride, chloride, nitrite, bromide, nitrate, phosphate and sulfate at 1, 2, 4, 4, 4, 6, and 4 ppm, respectively, for the high-level standard. This high-level standard was diluted 10 × to prepare the low-level standard. Tap water samples were directly injected and the wastewater sample was diluted 1:10 and filtered through a 0.45- μ m Millex HV filter before injection.

3. Results and discussion

3.1. Column and suppressor combinations

Three conventional anion-exchange columns, Waters IC Pak Anion HR, Sarasep AN 300 and Dionex AS4A-SC, were used in conjunction with an Alltech SPCS and Dionex AMMS. The HR column was used in both the non-suppressed and suppressed conductivity detection modes, while the AN 300 and AS4A columns were only used in the suppressed conductivity mode, as it has been previously established that such columns do not typically perform well in the non-suppressed mode [6]. Each column and suppressor combination was used to chromatograph a series of

injections of the high-level (1–6 ppm) standard, the low-level (0.1–0.6 ppm) standard, a tap water and a diluted wastewater sample. The linearity of each of the combinations was determined and the peak area repeatability was calculated from six replicate injections of the high-level anion standard. The 'sensitivity' of the various column, suppressor and hardware combinations was evaluated in terms of individual peak detection limits, rather than calculating sensitivity according to the correct definition of the term; that is as analyte response/concentration, e.g. in units of $\mu\text{V ml } \mu\text{g}^{-1}$ [7]. This approach was strictly a practical one, as the majority of analytical chromatographers use detection limits, rather than the slope of the analyte response/concentration curve, when considering system sensitivity. The detection limits were calculated (at a signal-to-noise of 3) from the chromatogram of the low-level anion standard for each of the column and suppressor combinations.

3.2. Non-suppressed ion chromatography

A borate–gluconate eluent was used with the HR column in the non-suppressed mode as this eluent has been shown to give the best overall separation selectivity for the common inorganic anions with methacrylate-based columns [6]. The background conductivity of the eluent was $283 \mu\text{S cm}^{-1}$ and low-pressure pulse dampeners were used with the pump, as specified by Waters [8]. Fig. 1a shows a chromatogram of a 100- μl injection of the low-level anion standard obtained using the borate–gluconate eluent with the HR column and conductivity detection. A poor baseline was obtained, which proved to be the result of the column not being placed in a temperature controlled environment. Fig. 1b shows the chromatogram of the low-level standard with the HR column maintained at 35°C in a column oven. The use of temperature control significantly improved the baseline and was crucial when performing non-suppressed IC analyses at sub-ppm levels. Heating the column at 35°C also affected the separation selectivity somewhat, i.e. retention times generally in-

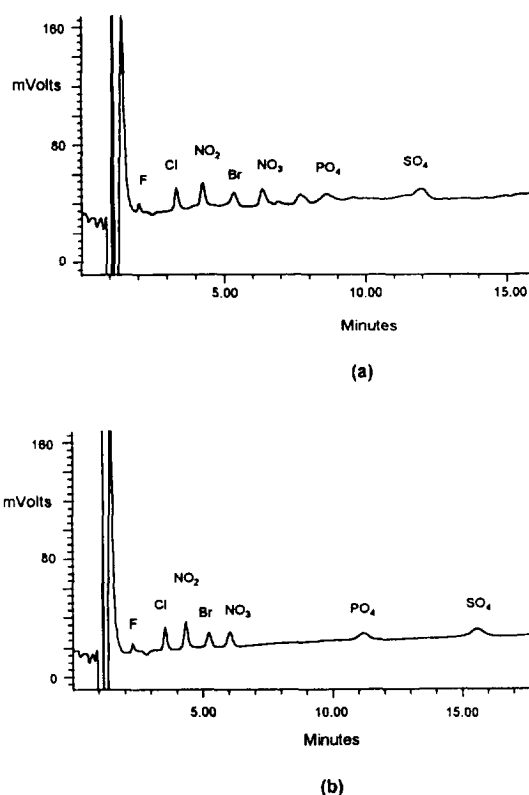


Fig. 1. Chromatogram of a low-level anion standard obtained using the HR column with non-suppressed conductivity detection. Conditions: column, Waters IC Pak Anion HR; eluent, borate–gluconate at 1.0 ml/min; injection volume, 100 μl ; detection, non-suppressed conductivity; column temperature, (a) ambient and (b) 35°C; solutes, 0.1–0.6 ppm as detailed in Experimental.

creased and the retention of sulfate and phosphate increased relative to the other peaks.

The tap water and 10 \times diluted wastewater samples were chromatographed using injection volumes of 100 and 50 μl , respectively. The results calculated for these two samples were generated using single-point calibration with the high-level anion standard, as was the case for all the other column and suppressor combinations. Both sample chromatograms showed the typical baseline disturbance which is characteristic of borate–gluconate eluents. This disturbance, or system peak, occurs from the presence of calcium and magnesium in the injected sample forming anionic complexes with the borate–gluconate diester [9] and elutes near the nitrate

Table 1
Tap water and wastewater sample results (ppm) obtained using each of the column and suppressor combinations

	HR	HR-S	HR-A	AN 300-S	AN 300-A	AS4A-S	AS4A-A
<i>Tap water</i>							
F	1.05	1.00	1.02	0.98	1.13	1.32	1.04
Cl	21.4	18.5	16.9	22.5	14.4	21.2	17.2
NO ₃	1.40	1.19	1.15	1.74	1.77	1.74	1.78
SO ₄	7.09	7.49	7.45	7.39	7.34	7.57	7.40
<i>Wastewater</i>							
F	12.8	9.78	11.7	9.18	11.1	12.32	8.55
Cl	17.3	13.3	14.4	16.4	11.8	21.4	13.7
NO ₃	3.97	4.73	6.84	4.07	4.23	4.73	4.12
SO ₄	796	893	801	823	787	846	785

HR = Waters HR column, AN 300 = Sarasep AN 300 column, AS4A = Dionex AS4A column, -S = Alltech SPCS, -A = Dionex AMMS.

peak. The presence of the system peak is a significant limitation of this mobile phase, as detection limits in real samples are typically not as good as for standards. This problem can be overcome by using a cation-exchange, hydrogen ion-donating device [10]; however, this adds additional sample preparation time (and expense) to the analysis. The sample results obtained using the HR column, and also those for each of the column and suppressor combinations, are given in Table 1.

Calibration curves were prepared for the HR column using a series of standards containing chloride, nitrate, phosphate and sulfate. The curves were prepared for each column and suppressor combination over as wide a concentration range as possible. Non-suppressed IC intrinsically gives linear calibration curves with conductivity detection [11] and the regression constants (r^2) were >0.9999 for all four solutes

with the HR column. The linearity data for the HR column, and for each of the column and suppressor combinations, is given in Table 2. Peak-area repeatability data were calculated for the HR column from six replicate injections of the high-level standard, with any obvious outliers being statistically rejected [12]. Table 3 summarises the peak-area repeatability data for the HR column, and for each of the column and suppressor combinations, while Table 4 shows the peak efficiency data, calculated using the half-height method, for the HR column and each of the other column and suppressor combinations. Method detection limits (signal-to-noise ratio of 3) were calculated from the chromatogram of low-level standard shown in Fig. 1b. Table 5 shows the detection limit (and baseline noise data) for each solute with the HR column, and also for each of the other column and suppressor combinations.

Table 2
Linearity data (regression constant, r^2) for each of the column and suppressor combinations

	HR	HR-S	HR-A	AN 300-S	AN 300-A	AS4A-S	AS4A-A
Cl	0.999975	0.999608	0.999798	0.999510	0.993370	0.999830	0.994999
NO ₃	0.999987	0.999263	0.999929	0.998778	0.998582	0.998856	0.998201
PO ₄	0.999974	0.999026	0.999955	0.999054	0.997979	0.998891	0.998827
SO ₄	0.999960	0.999568	0.999542	0.999677	0.999531	0.999656	0.999744

Column and suppressor identities as in Table 1.

Table 3
Peak-area repeatability data (% R.S.D.) for six replicate injections of the high-level anion standard for each of the column and suppressor combinations

	HR	HR-S	HR-A	AN 300-S	AN 300-A	AS4A-S	AS4A-A
F	1.167	1.010	2.151	3.250	1.672	28.559	2.725
Cl	0.588	0.553	2.302	1.795	0.520	1.782	0.204
NO ₂	0.553	1.929	0.729	3.573	0.974	2.270	0.429
Br	0.543	0.102	0.607	2.241	0.565	2.808	1.378
NO ₃	0.660	0.340	0.514	3.291	0.293	3.814	2.038
PO ₄	1.022	0.882	0.796	0.635	0.363	0.581	0.404
SO ₄	2.318	0.137	1.549	1.112	0.129	0.860	0.245

Column and suppressor identities as in Table 1.

Table 4
Peak efficiency (theoretical plates) data, averaged for six replicate injections of the high-level standard for each of the column and suppressor combinations, calculated using the half-height method

	HR	HR-S	HR-A	AN 300-S	AN 300-A	AS4A-S	AS4A-A
F	2618	1141	1114	2653	2489	944	712
Cl	2910	1872	1923	3074	3356	1656	1689
NO ₂	3029	1855	1737	3525	3381	1926	2158
Br	3377	2532	2578	4027	3595	3439	3428
NO ₃	3151	2613	2672	3402	3087	3012	2962
PO ₄	2475	2707	2660	4666	4394	3938	3898
SO ₄	3123	2882	2880	5262	5057	4888	4832

Column and suppressor identities as in Table 1.

3.3. Suppressed ion chromatography

All three columns, i.e. the HR, AN 300 and the AS4A, were then used in the suppressed mode with carbonate–bicarbonate eluents and

both the SPCS and AMMS devices. Fig. 2a shows a chromatogram of a 100- μ l injection of the low-level standard obtained using an eluent of 1.2 mM bicarbonate–1.2 mM carbonate at 1.0 ml/min with the HR column and the SPCS

Table 5
Detection limits (ppb) at a signal-to-noise ratio of 3 and baseline noise data (μ V) for each of the column and suppressor combinations

	HR (183 μ V)	HR-S (93 μ V)	HR-A (508 μ V)	AN 300-S (46 μ V)	AN 300-A (66 μ V)	AS4A-S (44 μ V)	AS4A-A (40 μ V)	HR-CatEx (33 μ V)
F	9.8	0.7	2.4	0.4	0.4	0.5	0.2	0.2
Cl	7.4	1.0	3.3	0.6	0.4	0.4	0.2	0.2
NO ₂	12.5	2.6	9.5	1.2	1.1	1.0	0.5	0.8
Br	23.2	4.5	16.4	2.1	2.1	1.5	0.9	1.4
NO ₃	22.7	4.3	15.6	2.0	2.0	1.3	0.8	1.3
PO ₄	75.2	10.5	37.4	4.3	3.9	4.0	2.6	2.6
SO ₄	40.4	4.2	17.5	1.8	1.7	1.7	1.2	1.4

Column and suppressor identities as in Table 1, except CatEx – cation-exchange suppressor.

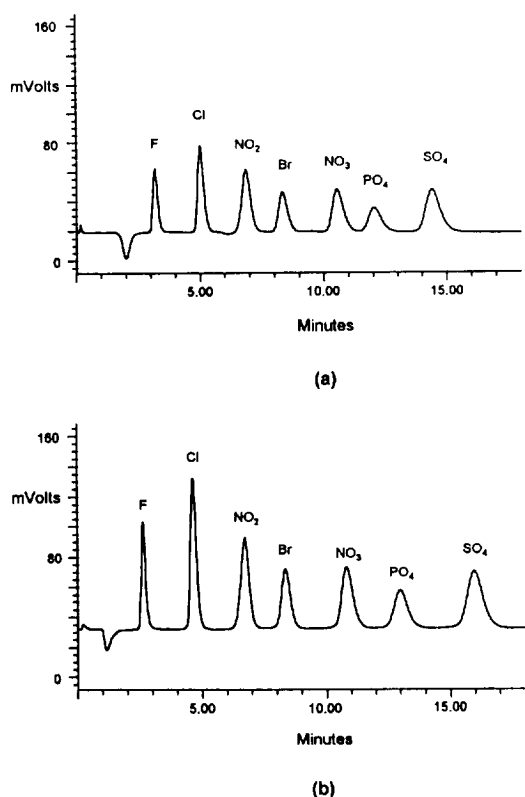


Fig. 2. Chromatogram of a low-level anion standard obtained using the HR column with suppressed conductivity detection. Conditions: column, Waters IC Pak Anion HR; eluent, 1.2 mM bicarbonate–1.2 mM carbonate at 1.0 ml/min; injection volume, 100 μ l; detection, suppressed conductivity using (a) SPCS and (b) AMMS suppressors; solutes, 0.1–0.6 ppm.

suppressor, while Fig. 2b shows the low-level standard chromatogram obtained using the same column and eluent with the AMMS suppressor. All the chromatograms for the low-level anion standards are shown using the same millivolt scale to allow direct comparison of the relative response for each column, eluent and suppressor combination. The overall selectivity of the methacrylate-based HR column was particularly good with the carbonate–bicarbonate eluent, i.e. the peaks were evenly resolved and fluoride was well separated from the column void.

The background conductivity of the 1.2 mM bicarbonate–1.2 mM carbonate eluent after suppression by the SPCS device was 17 and 25 μ S cm^{-1} after passing through the AMMS device.

The use of the low-pressure pulse dampeners proved crucial to obtaining a ‘pulseless’ baseline with both suppressor devices, as conductivity detectors are sensitive to even very minor pump pressure fluctuations, particularly at lower flow-rates. The addition of the pulse dampeners decreased the height of the baseline noise, from 1322 to 93 μ V for the SPCS device and from 1566 to 508 μ V for the AMMS device. A similar, although less drastic, effect was also seen with the HR column in the non-suppressed mode.

The AMMS device produced increased peak response relative to the SPCS device with the HR column; however, detection limits were lower with the latter combination due to the significantly lower ($\sim 5\times$) baseline noise. The greater peak response of the AMMS device was due to a combination of slightly lower dead volume and more efficient suppression in the micromembrane device. Perhaps surprisingly, both suppressor devices reduced peak efficiencies by approximately the same amount ($\sim 40\%$) for the early-eluting solute ions, as compared to the HR column in the non-suppressed mode. The use of the carbonate–bicarbonate eluent and suppressed conductivity detection resulted in calibration curves being somewhat less than linear with the HR column, although this eluent has an advantage over the borate–gluconate eluent for tap water and wastewater analysis in that no system peaks were observed. Also, bicarbonate present in the sample is not typically detected when using this mobile phase. The sample results, linearity, peak-area repeatability, peak efficiency and detection limit data for the HR column and both suppressor devices are shown in Tables 1–5, respectively.

Fig. 3a shows a chromatogram of a 100- μ l injection of the low-level anion standard obtained using an eluent of 1.7 mM bicarbonate–1.8 mM carbonate at 2.0 ml/min with the AN 300 column and the SPCS suppressor, while Fig. 3b shows the low-level standard chromatogram obtained using the same column and eluent with the AMMS suppressor. The background conductivity of the 1.7 mM bicarbonate–1.8 mM carbonate eluent after suppression by either the SPCS or the AMMS devices was 21 μ S cm^{-1} .

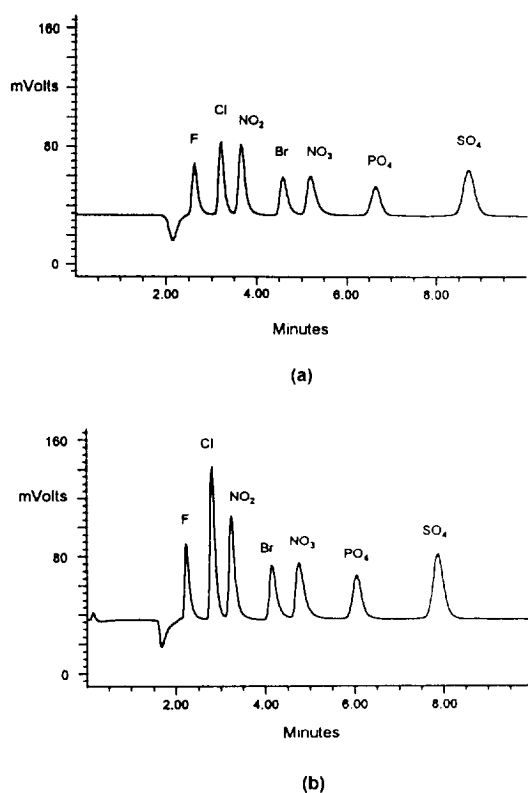


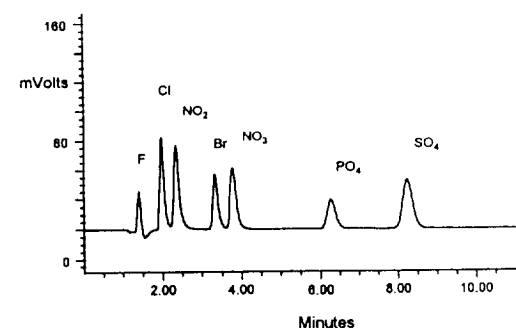
Fig. 3. Chromatogram of a low-level anion standard obtained using the AN 300 column with suppressed conductivity detection. Conditions: column, Sarasep AN 300; eluent, 1.7 mM bicarbonate–1.8 mM carbonate at 2.0 ml/min; injection volume, 100 μ l; detection, suppressed conductivity using (a) SPCS and (b) AMMS suppressors; solutes, 0.1–0.6 ppm.

The overall selectivity of the AN 300 column was not as good as the HR column and fluoride was not particularly well separated from the column void, however, the total run times were shorter. The addition of the pump pulse dampeners decreased the height of the baseline noise, by approximately $3\times$ for both suppressor devices, when using the AN 300 column. Both devices gave less baseline noise at a flow-rate of 2.0 rather than 1.0 ml/min, particularly the AMMS suppressor. Very similar detection limits resulted with the AN 300 column and either suppressor device. The higher efficiency of the AN 300 column, combined with the better operation of either suppressor device at 2.0 ml/min, resulted in detection limits being approximately $2\times$ lower

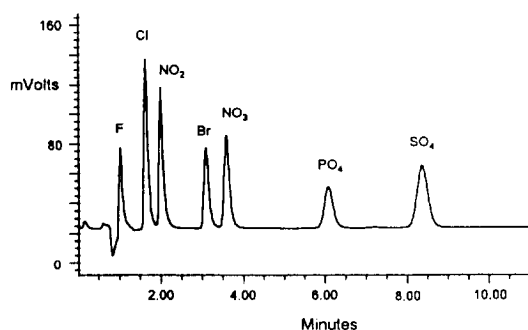
than with the HR column and the SPCS device combination.

Despite its proximity to the column void volume, the fluoride peak appeared sufficiently resolved from the void to allow quantitative determination in the tap water and wastewater samples. Generally, the results obtained for both samples using the AN 300 column were similar to those previously obtained with the HR column, except for chloride with the AMMS device. The AN-300 and the AMMS combination resulted in a calibration curve for chloride which significantly deviated from being linear, resulting in lower than expected sample results for chloride when quantitating using single-point calibration, as shown in Table 1. The sample results, linearity, peak-area repeatability, peak efficiency and detection limit data for the AN 300 column and both suppressor devices are shown in Tables 1–5, respectively.

Fig. 4a shows a chromatogram of a 100- μ l injection of the low-level anion standard obtained using an eluent of 1.7 mM bicarbonate–1.8 mM carbonate at 2.0 ml/min with the AS4A column and the SPCS suppressor, while Fig. 4b shows the low-level standard chromatogram obtained using the same column and eluent with the AMMS suppressor. Once again, the background conductivity of the 1.7 mM bicarbonate–1.8 mM carbonate eluent after suppression by either the SPCS or the AMMS devices was 21 μ S cm^{-1} . The overall selectivity of the AS4A column was very similar to that of the AN 300 column, although fluoride was not as well resolved from the column void. Once again, the addition of the pump pulse dampeners decreased the height of the baseline noise by approximately $3\times$ for both suppressor devices with the AS4A column. As was previously the case with the HR and AN 300 columns, the peak response with the AMMS device was greater than the SPCS device, due perhaps to more efficient suppression in the micromembrane device. Despite being slightly less efficient than the AN 300 column, the detection limits obtained with the AS4A were approximately $2\times$ lower than with the AN 300 column, due to the difference in column dimensions. The use of the 4.0 mm I.D. AS4A



(a)



(b)

Fig. 4. Chromatogram of a low-level anion standard obtained using the AS4A column with suppressed conductivity detection. Conditions as for Fig. 3, except the column (Dionex AS4A-SC).

column resulted in less peak dilution than the 7.8 mm I.D. AN 300 column, leading to greater peak response.

The combination of the AS4A column with the SPCS device did produce significant differences in fluoride results for both the tap water and wastewater samples. The peak area repeatability, shown in Table 3, for fluoride was also very poor as a result of the lack of resolution from the column void and the fact that the retention time of the void varied as a result of ion-exclusion effects within the packed-bed SPCS device [3]. However, the fluoride results obtained using the AS4A column and AMMS combination were similar to the those obtained previously, indicating that ion-exclusion effects within the SPCS device were leading to the poor fluoride results when it coupled with the AS4A

column. As was also the case with the AN 300 column, the use of the AS4A column and the AMMS device resulted in a calibration curve for chloride which significantly deviated from being linear, leading to lower than expected sample results for chloride when quantitating using single point calibration, as shown in Table 1. The sample results, linearity, peak-area repeatability, peak efficiency and detection limit data for the AS4A column and both suppressor devices are shown in Tables 1–5, respectively.

3.4. Alternative suppressor devices

Both the commercially available suppressor devices used in this work have their relative advantages and disadvantages. The SPCP utilises disposable cartridges which only have a finite lifetime. The cartridges are coated with an inert dye which provided a visible indication of the cartridge condition and gave a lifetime of only about 4 h with the 1.7 mM bicarbonate–1.8 mM carbonate eluent at 2.0 ml/min, although they had a lifetime of about 8 h when used with the 1.2 mM bicarbonate–1.2 mM carbonate eluent at 1.0 ml/min. Alternatively, the AMMS is continually regenerated, however, it required a large volume of dilute sulfuric acid along with a pneumatic reservoir and a gas supply. These problems were overcome with the recent introduction of a self-regenerating suppressor device, which requires no regenerant as it uses the electrolytic breakdown of water as a source of hydronium ions [13]. Despite the elegant advantage of continual regeneration, a disadvantage exists in that the membrane-based suppressors need to be replaced periodically as the membranes only have a finite lifetime. However, a much greater disadvantage is that it only takes one inappropriate sample or eluent to permanently damage a membrane-based device, while this is obviously of minimal concern when using disposable cartridges.

In principle, there is no need to use a specialised suppressor device for IC, as virtually any high-capacity cation exchanger can function as a suppressor. Fig. 5 shows a chromatogram of the

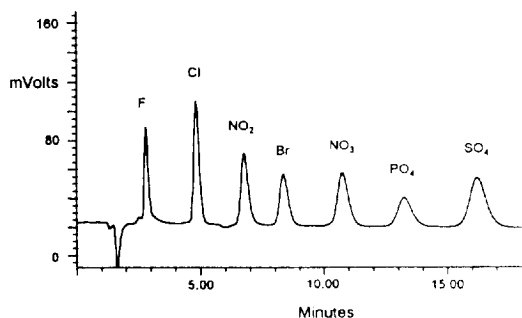


Fig. 5. Chromatogram of a low-level anion standard obtained using the HR column with a cation-exchange suppressor and conductivity detection. Conditions as for Fig. 2, except the detection method (suppressed conductivity using cation-exchange suppressor).

low-level anion standard obtained using a 1.2 mM bicarbonate–1.2 mM carbonate eluent at 1.0 ml/min with the HR column, conductivity detection and a 50×4.6 mm I.D. 'suppressor' column packed with sulfonated (2.0 mequiv./ml) polystyrene gel. The background conductivity of the eluent after suppression was $21 \mu\text{S cm}^{-1}$. In terms of peak response, this cation-exchange column was superior to the SPCS suppressor and very similar to the AMMS device. The combination of the less efficient HR column with the cation-exchange suppressor gave virtually identical detection limits to the combination of the more efficient AS4A column and AMMS, as shown in Table 5. The column could be used for approximately 8 h with the above eluent before regeneration (with 25 mM sulfuric acid) was required. An attempt to use a still higher-capacity (5.0 mequiv./g) cation-exchange column (Waters Fast Fruit Juice) as a suppressor met with mixed success. This column was the best of all the suppressor devices investigated, in terms of peak response, however, ion-exclusion effects resulted in nitrite being eluted as a negative peak. As this column was specifically intended for use as an ion-exclusion column, it was hardly surprising that exclusion effects were prominent. Therefore, selecting an appropriate cation exchanger to function as a suppressor for anion analysis should simply be a matter of choosing a column with good chromatographic efficiency,

high cation-exchange capacity and minimum exclusion effects.

In terms of an optimal system configuration for the IC analysis of anions in water and wastewater samples, a dual-piston pump equipped with low-pressure pulse dampeners should be used to minimise baseline fluctuations. The use of a methacrylate-based anion-exchange column permits the best overall separation selectivity with a carbonate–bicarbonate eluent, while a solid-phase cation-exchange suppressor and conductivity detector offer the best detection compromise in terms of sensitivity, linearity and analytical sample performance.

4. Conclusions

A number of conclusions relating to optimising system performance and sensitivity in IC are evident from this study. The use of a dual-piston pump equipped with low-pressure pulse dampeners will minimise baseline noise when using conductivity detection. Column temperature control was essential in order to achieve routine sub-ppb detectability in non-suppressed IC, although temperature control appeared to make little difference for suppressed IC.

In general, the use of suppressed IC resulted in significantly lower (5–10 \times) detection limits than non-suppressed IC when using the same columns and hardware, with the methacrylate-based HR column giving the best overall separation selectivity when using a carbonate–bicarbonate eluent and suppressed conductivity detection. Both the SPCS and the AMMS suppressor devices gave similar performance in terms of band broadening, with the latter resulting in slightly improved peak response. Not all the column and suppressor combinations studied gave satisfactory results: the AMMS device resulted in excessive baseline noise when used at the flow-rates required for the HR column, while the combination of the AS4A column and SPCS resulted in unacceptable results for fluoride. The use of the AMMS device with the AN-300 and AS4A columns gave the least linear calibration curves, particularly for chloride, resulting in

lower than expected analytical results for chloride when quantitating using single point calibration.

In addition to the use of commercially available suppressor devices, there is also a large number of high-capacity cation exchangers which can be used as suppressors. These columns may, in some instances, offer equivalent (or superior) performance when compared to the commercial devices and it appears that an appropriate solid-phase cation-exchange suppressor may well offer the best compromise for suppressed conductivity detection in terms of sensitivity, linearity and analytical performance.

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