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## Recent advances in ion chromatography suppressor improve anion separation and detection

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### Abstract

The Alltech DS-Plus suppressor improves and simplifies anion analysis by suppressor-based ion chromatography (IC). In addition to suppressing the mobile phase and enhancing the analyte signal, the DS-Plus suppressor removes carbonic acid from the suppressor effluent when carbonate–hydrogencarbonate mobile phases are used, reducing the water dip that interferes with early eluting peaks, increasing detection sensitivity, and enabling carbonate–hydrogencarbonate gradients. The ability to operate with carbonate–hydrogencarbonate gradients places exceptional separating power in the mobile phase, forgoing the need for expensive columns with special selectivity. Continuous operation and solid-phase chemistry eliminates the need for external regenerants, switching valves, and multiple operating modes. © 2002 Elsevier Science B.V. All rights reserved.

*Keywords:* Suppressors; Ion chromatography; DS-Plus suppressor; Inorganic anions

### 1. Introduction

Since its introduction in 1975, many advances in ion chromatographic (IC) separation and detection have been reported. Some of these are described in several books and papers [1–6]. Some of the most important advances relate to suppressor development [7–9]. Suppressors are used in conjunction with conductivity detectors to improve detection sensitivity, especially for anion analysis.

Two suppressor types are commonly used for anion analysis. They are continuously regenerated membrane suppressors and intermittently regenerated packed-bed suppressors. Electrochemical and chemi-

cal regeneration have been used with both. Packed-bed suppressors are more rugged and reliable than membrane suppressors [8], but intermittent regeneration limits run time and requires mechanical switching mechanisms. While more fragile, membrane suppressors offer continuous operation and regeneration.

This paper describes a new packed bed suppressor (DS-Plus suppressor<sup>1</sup>) that is continuously regenerated electrochemically. The new device tolerates high backpressures, does not require water or regenerant delivery systems, and has no switching valves or other mechanical components. In addition to suppressing the mobile phase and enhancing the analyte signal through acid–base neutralization re-

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<sup>1</sup>Patents pending.

actions like traditional IC suppressors, this new suppressor also removes carbonic acid as  $\text{CO}_2(\text{g})$  from the analyte stream, reducing background conductivity with carbonate–hydrogencarbonate mobile phases to near zero. This improves the signal-to-noise ratio, reduces the water dip that often interferes with early eluting peaks, and enables gradient separations with carbonate–hydrogencarbonate mobile phases with minimal baseline shift.

## 2. Experimental

An Alltech (Deerfield, IL, USA) ion chromatograph consisting of a model 526 HPLC pump, Model 570 autosampler, Model 530 column heater, DS-Plus suppressor, and Model 650 conductivity detector was used. The Dionex (Sunnyvale, CA, USA) ASRS membrane suppressor was used to obtain comparison data. The Dionex IonPac AS4A-SC and AS9-HC were used for anion separations. All data were recorded using the AllChrom data station from Alltech.

Anion and cation standards were prepared by diluting 200 mg/l certified IC standards from Alltech. Mobile phases were prepared using the Alltech EZ-LUTE buffer concentrates. All solutions were prepared with de-ionized water.

## 3. Results and discussion

In previous research, we reported that when an electric field is applied across two electrodes sandwiching ion-exchange resins, current is carried across the resin with low resistance [4,8]. This discovery resulted in the development of the electrochemically regenerated packed bed-suppressor (Alltech ERIS 1000 Auto Suppressor). The electrochemical regeneration eliminates the need for regenerant reagent and equipment. The packed-bed chemistry tolerates high back pressure, organic solvents, and electroactive mobile phases. Two suppressor cells and a switching valve were required in the instrument for continuous, uninterrupted operation. While one cell was used for suppression, the other was regenerated and equilibrated.

In the DS-Plus suppressor, the cell configuration

was modified so that it operates continuously without the need for switching valves or other switching mechanisms. It is the first packed-bed suppressor that operates continuously, and is the first suppressor that operates without external regenerants, external water supplies, or the detector effluent under all operating conditions. After mobile phase suppression, the DS-Plus suppressor removes dissolved carbon dioxide from the suppressor effluent. This process reduces the water dip that interferes with early-eluting peaks, increases detection sensitivity, and enables a powerful carbonate–hydrogencarbonate gradient [10].

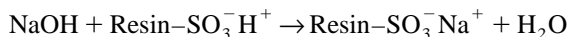
Fig. 1 shows the suppressor cell configuration in the DS-Plus suppressor. After entering the cell, the mobile phase and sample ions split proportionally between three cell exits; one through the anode, one through the cathode, and one leading to the detector. Since conductivity detector response is proportional to concentration, not absolute mass, sending only a portion of suppressor effluent to the detector has no affect on detection sensitivity because sample concentration does not change as a result of the split.

Three processes occur simultaneously in the suppressor: continuous suppression, electrochemical regeneration, and gas removal.

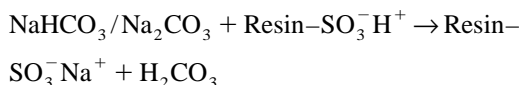
### 3.1. Continuous suppression

Inside the suppressor cell, the mobile phase and sample ions from the analytical column undergo an acid–base neutralization reaction. The cell is packed with a strong cation-exchanger in the hydrogen form. The following reactions take place in the suppressor cell:

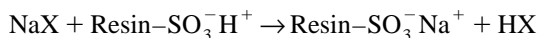
Mobile phase:



or



Sample:



X = anions ( $\text{Cl}^-$ ,  $\text{NO}_3^-$ ,  $\text{Br}^-$ , etc.)

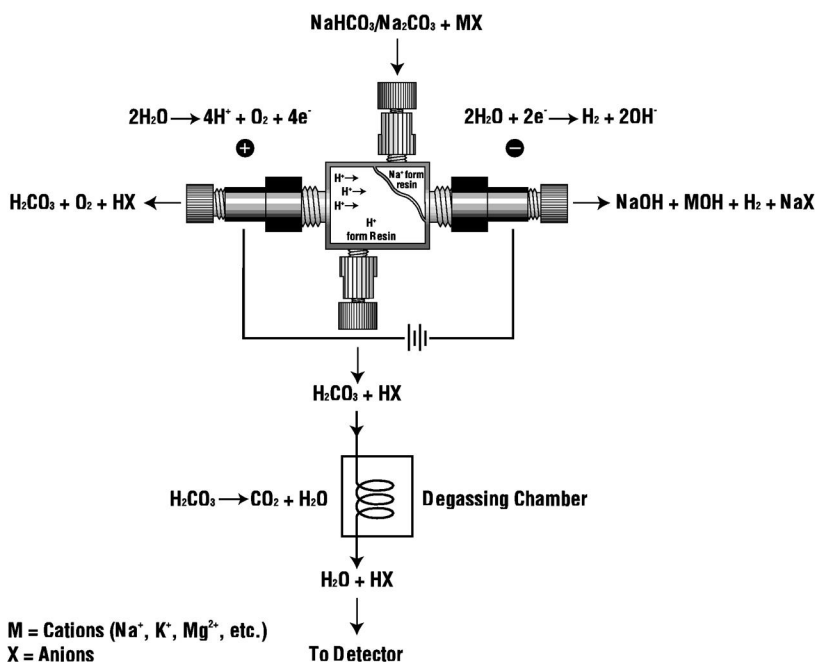
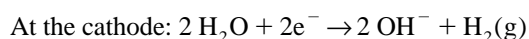
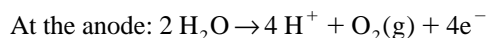


Fig. 1. Suppressor cell configuration in the DS-Plus suppressor.

The counter ions ( $\text{Na}^+$ ) from the mobile phase are exchanged with the hydrogen ions ( $\text{H}^+$ ) in the cell to form water if hydroxide is used as the mobile phase, or carbonic acid if carbonate–hydrogencarbonate is used as the mobile phase. Simultaneously, the counter cations from the sample are exchanged with the hydrogen ions in the cell. The released hydrogen ions react with sample anions to form highly conductive acids (i.e. hydrochloric acid, nitric acid, etc). The result is a higher signal-to-noise ratio and improved detection sensitivity. These reactions occur in all anion IC suppressors.

### 3.2. Electrochemical regeneration

The power supply in the DS-Plus suppressor applies current continuously across the suppressor cell during operation as long as there is liquid flow through the cell. Water in the cell undergoes electrolysis as follows:



At the anode, hydrogen ions and oxygen gas are generated. At the cathode, hydroxide ions and hydrogen gas are generated. The hydrogen ions generated at the anode flow across the cation-exchange packing, forcing the sodium ions from the mobile phase and cations from the sample toward the cathode. Hydroxide and/or carbonate salts, hydrogen gas, and a portion of the sample anions (sodium form) exit through the cathode. Carbonic acid or water, oxygen gas, and a portion of the sample anions (acidic form) exit through the anode. Carbonic acid or water and a portion of the sample anions (acidic form) exit through the detector outlet.

The DS-Plus instrument is designed so that the current to the suppressor cell is applied only when there is liquid flow through the cell. The current is automatically shut down when there is no flow through the cell.

### 3.3. Gas removal

Before reaching the detector, the cell effluent containing the sample anions and carbonic acid (if carbonate–hydrogencarbonate is used as the mobile

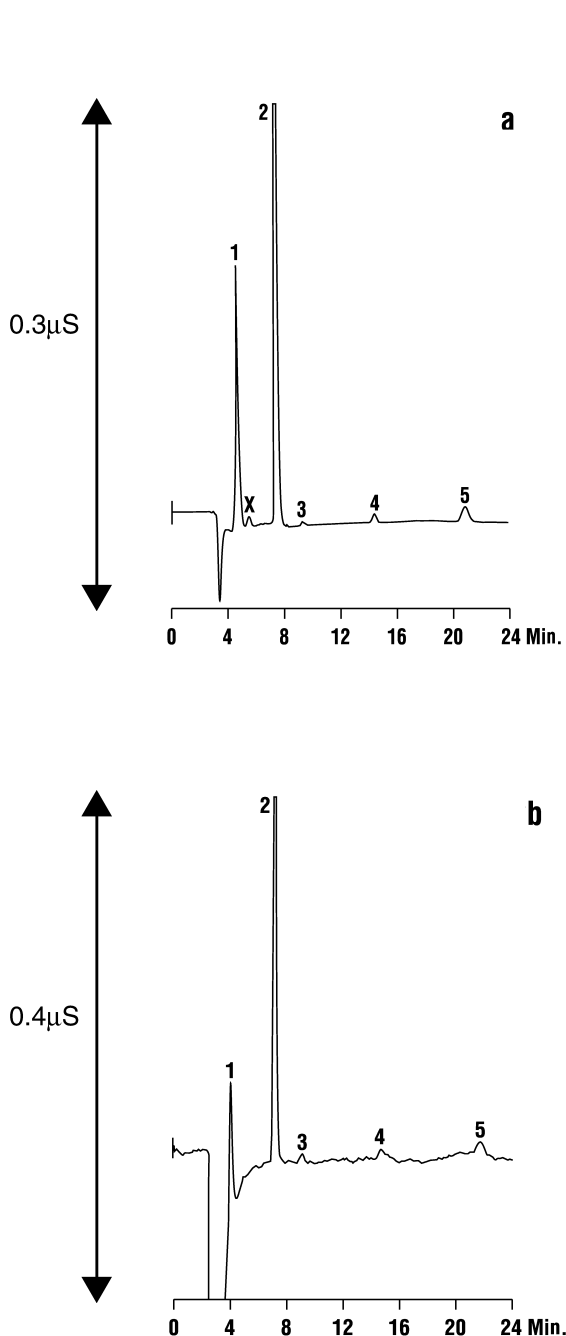


Fig. 2. Trace anions in water. (a) With DS-Plus suppressor; (b) with ASRS suppressor, external water mode. Peak identification: 1=fluoride (83  $\mu\text{g/l}$ ), 2=chloride (210  $\mu\text{g/l}$ ), 3=Nitrite (3  $\mu\text{g/l}$ ), 4=Nitrate (12  $\mu\text{g/l}$ ), 5=Sulfate (16  $\mu\text{g/l}$ ), X=unknown. Column: AS9-HC, 250 $\times$ 4.0 mm; mobile phase: 9.0 mM  $\text{Na}_2\text{CO}_3$ ; flow-rate, 1.0 ml/min; detection: suppressed conductivity; injection volume, 200  $\mu\text{l}$ .

phase) enters a degassing chamber for gas removal (US patents Nos. 5,006,382; 5,340,384; others pending). The suppressor effluent flows through a tubular degassing membrane. Carbonic acid in the suppressor effluent dissociates to form carbon dioxide and water:



The carbon dioxide gas diffuses across the degassing membrane, driving the equilibrium of the above reaction to the right, producing more carbon dioxide gas. This process removes substantially all the carbonic acid from the suppressor effluent, leaving water and acid-form sample anions in liquid stream reaching the detector. Removing carbonic acid reduces background conductivity from approximately 20  $\mu\text{S}$  to about 1–2  $\mu\text{S}$  (varies depending on the carbonate concentration). As a result, detection sensitivity and baseline stability are improved and the water dip, which often interferes with early-eluting peaks, is eliminated or substantially reduced. Finally, carbonate–hydrogencarbonate gradients may be used because background conductivity remains constant as carbonate–hydrogencarbonate concentration changes.

The gas removal feature of the DS-Plus suppressor sets it apart from all other IC suppressors. Fig. 2 shows chromatograms of trace anions in high-purity water obtained using the DS-Plus suppressor and a membrane suppressor. Because the DS-Plus suppressor converts the background solution from carbonic acid to water (the background conductivity decreased from about 15  $\mu\text{S}$  to about 1  $\mu\text{S}$ ), the size of the water dip is reduced significantly. With the membrane suppressor, the large water dip interferes with fluoride quantification, and the signal-to-noise ratio is lower than with the DS-Plus suppressor.

Fig. 3 shows another application where the size of the water dip is significantly reduced with the DS-Plus suppressor. US Environmental Protection Agency (EPA) Method 300.1, part B specifies a 200  $\mu\text{l}$  injection volume. With larger injection volumes, the water dip increases, interfering with early-eluting peaks. Because the DS-Plus suppressor reduces the water dip, larger injection volumes may be used to increase detection sensitivity, without sacrificing the measurement accuracy of the early-eluting peaks [11].

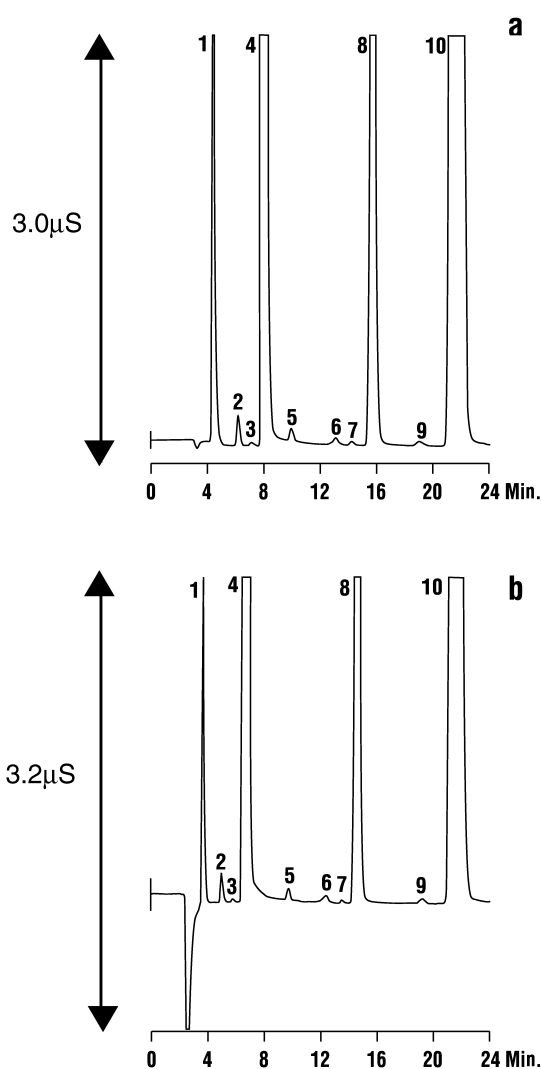


Fig. 3. Inorganic anions and oxyhalides (EPA method 300.1, Part B). (a) With DS-Plus suppressor; (b) with ASRS suppressor, recycle mode. Peak identification: 1=fluoride (1 mg/l), 2=chlorite (0.5 mg/l), 3=bromate (0.05 mg/l), 4=chloride (50 mg/l), 5=Nitrite (0.1 mg/l), 6=bromide (0.05 mg/l), 7=chlorate (0.05 mg/l), 8=Nitrate (10 mg/l), 9=phosphate (0.1 mg/l), 10=sulfate (50 mg/l). Column: AS9-HC, 250×4.0 mm; mobile phase: 9.0 mM  $\text{Na}_2\text{CO}_3$ ; flow-rate: 1.0 ml/min; detection: suppressed conductivity; injection volume: 200  $\mu\text{l}$ .

Previously, gradient elution in IC with conductivity detectors was limited to sodium hydroxide and/or sodium tetraborate mobile phases. Sodium hydroxide is converted to water in the suppressor, producing a constant, near zero background con-

ductivity during gradient runs. Carbonate–hydrogencarbonate is the preferred mobile phase for anion analysis because it contains both monovalent and divalent ions for greater selectivity control compared to hydroxide mobile phases. Adjusting the carbonate–hydrogencarbonate ratio in the mobile phase is a powerful way to control separation selectivity and speed, a technique not available with hydroxide mobile phases. However, carbonate–hydrogencarbonate mobile phases may not be used for gradient elution with conventional suppressors because the carbonic acid suppressor effluent has measurable background conductivity. The background signal increases with carbonate–hydrogencarbonate concentration because the amount of carbonic acid reaching the detector also increases (Fig. 4b). The DS-Plus suppressor removes carbonic acid before detection, reducing baseline shift during carbonate–hydrogencarbonate gradients to acceptable levels (Fig. 4a).

The DS-Plus suppressor streamlines IC methods and lowers operating costs. In most cases, powerful carbonate–hydrogencarbonate mobile phases (isocratic or gradient) perform even complex separations with one or two column chemistries. Special columns or mobile phases are not required. Only one operating mode is used with the DS-Plus suppressor, even with organic-containing or electroactive mobile phases because electrolysis byproducts exit the DS-Plus cell through the anode and cathode and never reach the detector. No regenerants, external water supplies, or the associated pumps and plumbing are required, even for trace level works. With ASRS membrane suppressors, the external water mode is recommended for trace-level analysis because it produces lower baseline noise [12,13].

Fig. 5 shows two gradient separations performed with a standard Dionex IonPac AS4A column, carbonate–hydrogencarbonate mobile phases and the DS-Plus suppressor. The separation of weak and strong acid anions previously required a specialized column (Dionex IonPac AS14), a sodium tetraborate gradient, and a membrane suppressor (ASRS) operated in the “external water” mode [14]. The separation of common anions plus iodide, thiosulfate, and thiocyanate, previously required a specialized column (Dionex IonPac AS11) a sodium hydroxide and methanol gradient, and a ASRS suppressor with an external chemical regenerant (sulfuric acid) [15]. The

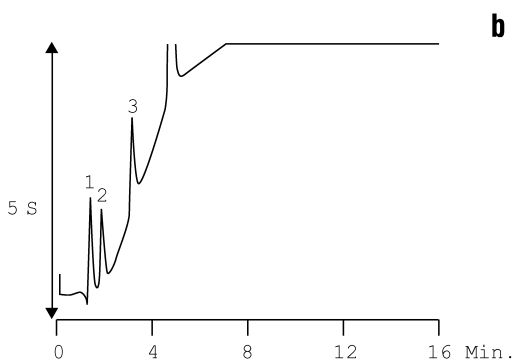
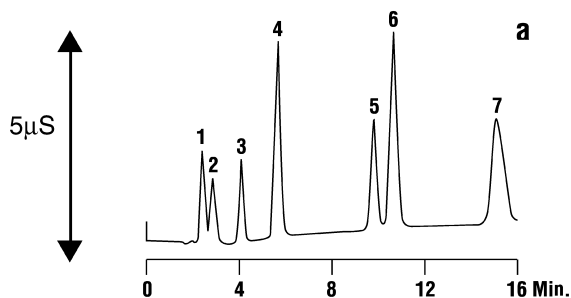


Fig. 4. Multivalent anions. (a) With DS-Plus suppressor; (b) with ASRS suppressor, external water mode. Peak identification: 1 = fluoride (2 mg/l), 2 = chloride (2 mg/l), 3 = nitrate (5 mg/l), 4 = phosphate (10 mg/l), 5 = iodide (20 mg/l), 6 = thiocyanate (20 mg/l), 7 = thiosulfate (20 mg/l). Column: AS4A-SC, 250×4.0 mm; mobile phases: (A) water, (B) 10 mM sodium carbonate, 1 mM cyanophenol; gradient: 30–50% B in 3 min, to 70% B in 12 min, to 30% B in 2 min. Flow-rate: 1.5 ml/min; detection: suppressed conductivity; injection volume: 25  $\mu$ l.

chemical regenerant was necessary with the ASRS suppressor because electrochemical regeneration is not compatible with organic solvents [7]. In both of these situations, additional equipment and reagents were required to deliver water or sulfuric acid to the suppressor's regenerant channel.

The DS-Plus suppressor equilibrates quickly under any conditions. It has been reported that with the ASRS membrane suppressor, it takes longer to equilibrate, especially when analyzing anions at trace level [13,16].

### 3.4. Reproducibility, efficiency and detection limits

The retention time and peak area reproducibility

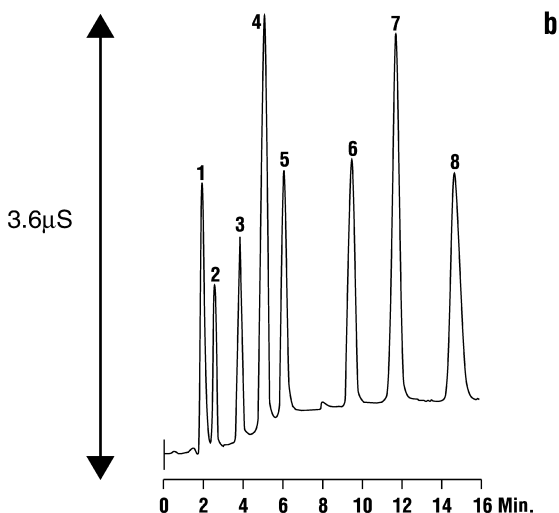
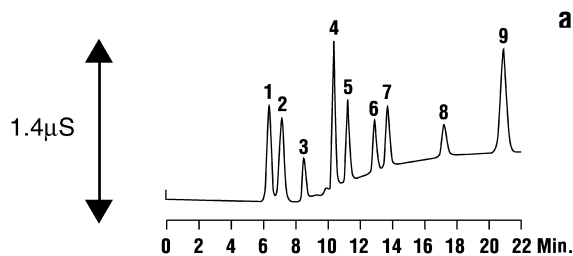


Fig. 5. (a) Weak and strong acid anions. Peak identification: 1 = fluoride (2 mg/l), 2 = acetate (10 mg/l), 3 = formate (2 mg/l), 4 = chloride (4 mg/l), 5 = nitrite (4 mg/l), 6 = bromide (4 mg/l), 7 = nitrate (4 mg/l), 8 = phosphate (6 mg/l), 9 = sulfate (6 mg/l). Column, AS4A-SC, 250×4.0 mm; mobile phases: (A) Water, (B) 5 mM sodium hydrogencarbonate, (C) 5 mM sodium carbonate; gradient: 0% B and C to 0% B and C in 5 min, to 34% B and 36% C in 3 min, to 44% B and 56% C in 2 min, to 44% B and 56% C in 15 min, to 0% B and C in 0.1 min. Flow-rate: 1.0 ml/min; detection: suppressed conductivity; injection volume: 25  $\mu$ l. (b) Common anions including iodide, thiosulfate, and thiocyanate. Peak identification: 1 = fluoride (2 mg/l), 2 = chloride (2 mg/l), 3 = nitrate (5 mg/l), 4 = phosphate (10 mg/l), 5 = sulfate (5 mg/l), 6 = iodide (20 mg/l), 7 = thiocyanate (20 mg/l), 8 = thiosulfate (20 mg/l). Column: AS4A-SC, 250×4.0 mm; mobile phases: (A) 5 mM sodium hydrogencarbonate, (B) 5 mM sodium carbonate, 1 mM cyanophenol; gradient: 44% B to 100% B in 5 min, to 100% B in 20 min, to 44% B in 0.1 min. Flow-rate: 1.5 ml/min; detection: suppressed conductivity; injection volume: 25  $\mu$ l.

for 30 consecutive injections of anions in the low mg/l range on the DS-Plus IC system are listed in Tables 1 and 2, respectively. The retention time relative standard deviation (RSD) for all anions is under 0.6%. The peak area RSD is under 2%. These

Table 1  
Retention time reproducibility for 30 consecutive injections

Anion	Average retention time (min)	RSD (%)
Fluoride (2 mg/l)	3.02	0.58
Chloride (4 mg/l)	3.98	0.54
Nitrite (4 mg/l)	4.56	0.52
Bromide (4 mg/l)	6.24	0.56
Nitrate (4 mg/l)	6.96	0.54
Phosphate (6 mg/l)	10.65	0.31
Sulfate (6 mg/l)	13.40	0.30

Table 2  
Peak area reproducibility for 30 consecutive injections

Anion	Concentration (mg/l)	RSD (%)
Fluoride	2	1.9
Chloride	4	2.0
Nitrite	4	1.7
Bromide	4	1.4
Nitrate	4	1.5
Phosphate	6	1.7
Sulfate	6	1.5

values are comparable to the values obtained using other suppressors [17].

The chromatographic efficiency, expressed as number of theoretical plates per column, is listed in Table 3. The DS-Plus suppressor produces slightly better efficiency than the membrane suppressor. These values were obtained using a AS9-HC, 250 ×

Table 3  
Peak efficiencies (number of theoretical plates/column) using the DS-Plus suppressor and membrane suppressor

Anion	Peak efficiency	
	DS-Plus suppressor	Membrane suppressor
Fluoride	3253	2366
Chloride	6595	5328
Nitrite	6936	6266
Bromide	8633	8095
Nitrate	9062	8400
Phosphate	7234	6959
Sulfate	8775	7702

Table 4  
Method detection limit for anions with the DS-Plus suppressor

Anion	Method detection limits <sup>a</sup> (ppb)
Fluoride	0.3
Chloride	0.6
Nitrite-N	0.9
Bromide	2.8
Nitrate-N	0.4
Phosphate-P	1.4
Sulfate	1.2

<sup>a</sup> MDL calculated as the  $SD/\sqrt{3.142}$  (for seven replicate injections). Column: AS9-HC, 250 × 4.0 mm; mobile phase: 9 mM  $\text{Na}_2\text{CO}_3$ ; injection volume: 100  $\mu\text{l}$ .

4.0 mm column, and 9 mM sodium carbonate mobile phase at 1.0 ml/min.

Fig. 6 shows calibration curves for nitrite, bromide, and sulfate. Detector response is linear for

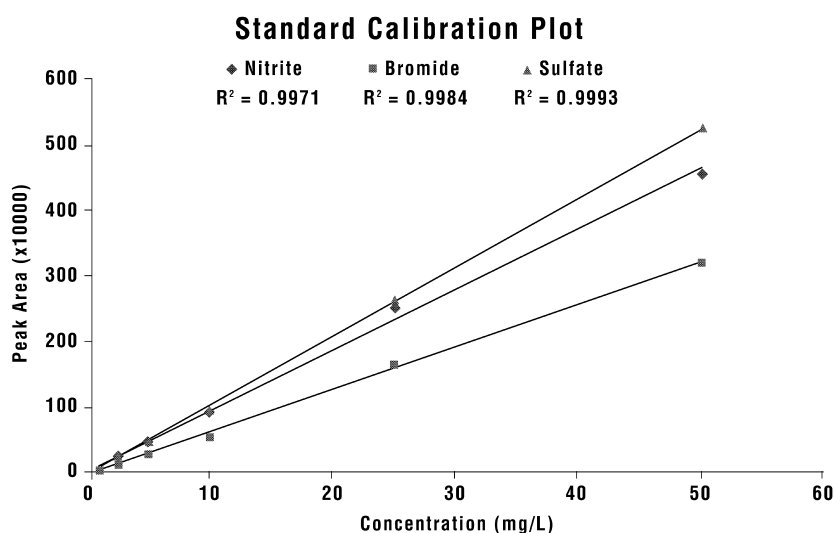


Fig. 6. Calibration plots of peak area vs. concentration for nitrite, bromide, sulfate.

these three analytes with correlation coefficients near unit. Detection limits (MDL) for seven common anions are listed in Table 4. These values are better than those reported in EPA Method 300.1 [18].

#### 4. Conclusion

The DS-Plus suppressor improves and simplifies suppressor-based anion analysis methods. When carbonate–hydrogencarbonate mobile phases are used, the DS-Plus suppressor removes carbonic acid from the suppressor effluent, substantially reducing the water dip that interferes with early eluting peaks, increasing detection sensitivity, and enabling carbonate–hydrogencarbonate gradient. The ability to operate with carbonate–hydrogencarbonate gradients places exceptional separating power in the mobile phase, forgoing the need for expensive columns with special selectivity. Continuous operation and solid-phase chemistry eliminates the need for regenerants, switching valves, and multiple operating modes.

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