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## New suppressor technology improves trace level anion analysis with carbonate–hydrogencarbonate mobile phases

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### Abstract

Sodium carbonate–hydrogencarbonate mobile phases are preferred over sodium hydroxide for anion analysis by suppressor-based ion chromatography (IC). Unlike hydroxide, carbonate–hydrogencarbonate has strong eluting power and its buffering capacity can be used as a selectivity tool for controlling separations. However, carbonate–hydrogencarbonate mobile phases fell out of favor for trace level analysis because the carbonic acid suppressor effluent has some background conductivity, which reduces sensitivity compared to sodium hydroxide. This paper describes a new suppressor technology that improved anion analysis with carbonate–hydrogencarbonate mobile phases. In addition to converting the carbonate–hydrogencarbonate buffer to carbonic acid like other traditional IC suppressors, the new DS-Plus suppressor also removed carbonic acid from the suppressor effluent. Anions are now detected in water background, just like when using sodium hydroxide as the mobile phase. The lower background conductivity improves sensitivity and reduces detection limits. The water-dip often seen with conventional suppressors is greatly reduced, improving fluoride quantification. © 2002 Elsevier Science B.V. All rights reserved.

*Keywords:* Ion chromatography; Mobile phase composition; Inorganic anions

### 1. Introduction

In anion analysis, suppressors are used to increase detection sensitivity with conductivity detectors. The suppressor function is to reduce the background conductivity of the mobile phase before it enters the conductivity detector [1]. As the suppressor reduces the mobile phase conductivity, it increases the conductivity of the analyte. Suppressors increase the signal-to-noise ratio about one order of magnitude for strong acids and slightly less for weak acids [2]. The increased sensitivity makes suppressors a requirement for trace level anion analysis.

Methods using direct injection of large sample

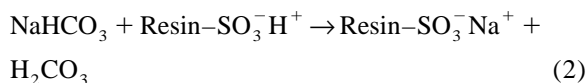
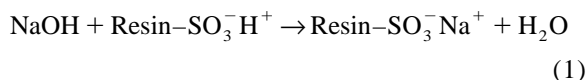
volumes have been developed to improve trace level analysis [3,4]. These methods have successfully been used to analyze anions in the low  $\mu\text{g}/\text{l}$  to high  $\text{ng}/\text{l}$  concentration range. High-volume direct injection methods do not need preconcentration and the required equipment that add cost and complexity to the system. Methods for this type of analysis have been developed using high-purity hydroxide as the mobile phase [4–6].

The choice of mobile phase will affect the resolving power of the column and the background conductivity of the mobile phase after suppression. The two most common mobile phases for anion analysis are sodium hydroxide and sodium carbonate–sodium hydrogencarbonate. Sodium hydroxide is classified as having weak elution strength while sodium carbonate–sodium hydrogencarbonate has medium to

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strong elution strength [1]. Both mobile phases have greatly reduced background conductivities after suppression:



Sodium hydroxide has much lower background conductivity than sodium carbonate–sodium hydrogencarbonate after suppression because the product of the sodium hydroxide suppression is water, which has little or no conductivity. The product of sodium carbonate–sodium hydrogencarbonate suppression is carbonic acid, which is weakly conductive. The lower conductivity of water gives a higher signal-to-noise ratio, making sodium hydroxide the preferred mobile phase for trace level anion analysis.

New suppressor technology is described here that improves trace level anion analysis with sodium carbonate–sodium hydrogencarbonate mobile phases. The Alltech DS-Plus suppressor degasses the suppressor effluent before detection [7], removing carbon dioxide and leaving water as the suppressor product. Post-suppression degassing was originally reported in the 1980s, but the techniques were impractical for routine use due to band broadening, membrane-suppressor pressure limitations, and chemical resistance constraints [8,9]. The DS-Plus suppressor overcomes these limitations through the use of highly efficient, low dead-volume, chemically resistant degassing tubing. The background conductivity is reduced, and the baseline becomes smoother. The signal-to-noise ratio and sensitivity are improved over other suppressors. The degassing also greatly reduces the water dip that can cause interference with early eluting analytes.

## 2. Experimental

The chromatography system used was an Alltech (Deerfield, IL, USA) ion chromatograph consisting of a Model 526 HPLC pump, Model 570 auto-sampler, Model 530 column heater, DS-Plus suppressor,

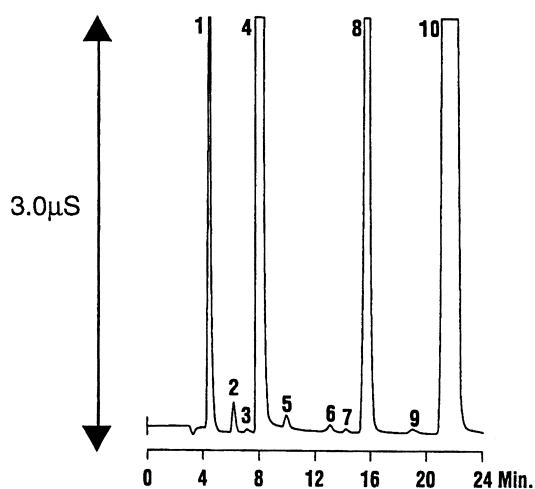
Model 550 conductivity detector, and a Model 650 conductivity detector. The Dionex (Sunnyvale, CA, USA) ASRS membrane suppressor was used to obtain comparison data. The Dionex IonPac AS4A-SC (250×4.0 mm) and AS9-HC (250×4.0 mm) and Alltech Novosep A-1 (150×4.6 mm) were used for anion separations. All data were recorded using the AllChrom data station.

Anion standards were prepared by diluting 200 mg/l certified ion chromatography (IC) standards from Alltech. Mobile phases were prepared using the Alltech EZ-LUTE buffer concentrates of 500 mN NaHCO<sub>3</sub> and 500 mM Na<sub>2</sub>CO<sub>3</sub>. All solutions were prepared with deionized water.

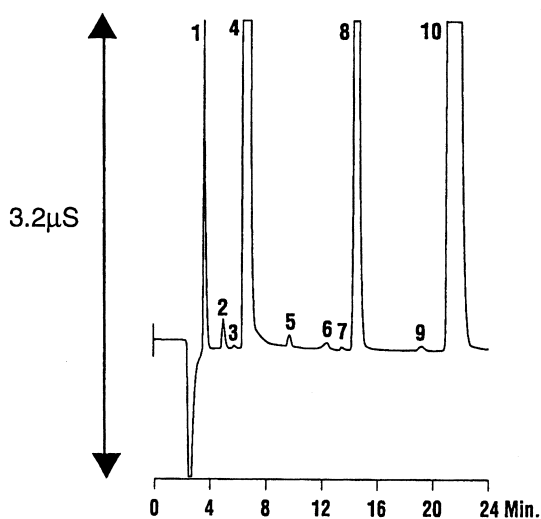
## 3. Results and discussion

With conventional IC suppressors, carbonate–hydrogencarbonate mobile phases generate large water dips in the beginnings of chromatograms. The water dips are formed from the water eluting off the column having a lower conductance than the background of the suppressed mobile phase (carbonic acid). Larger injection volumes contain more water and give much larger water dips. The DS-Plus suppressor degasses the suppressor effluent before it enters the conductivity detector [7]. This process removes the dissolved carbon dioxide from the suppressor effluent, leaving water as the background for detection. The drop in background conductivity due to degassing reduces the size of the water dip significantly. Fig. 1a and 1b compare a 200-μl injection of the seven common anions and disinfection byproducts obtained per United States Environmental Protection Agency (EPA) method 300.1 with DS-Plus suppressor and Dionex ASRS suppressors. The analysis with DS-Plus suppressor gives a much smaller water dip with a background of 1 μS than the Dionex ASRS suppressor with a background of 15 μS.

The large water dip found with carbonate–hydrogencarbonate mobile phases and conventional suppressors can interfere with early eluting peaks such as fluoride. The DS-Plus suppressor eliminates this interference by reducing the size of the water dip, as shown in Fig. 2a. In Fig. 2b, where the chromato-



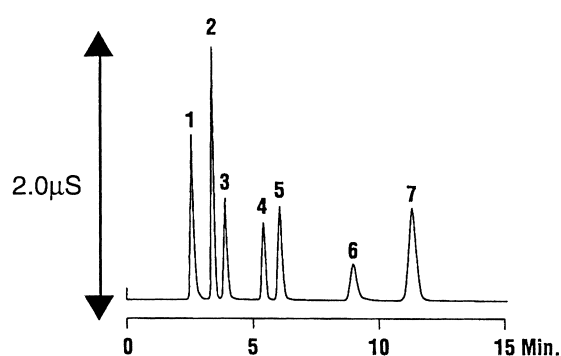
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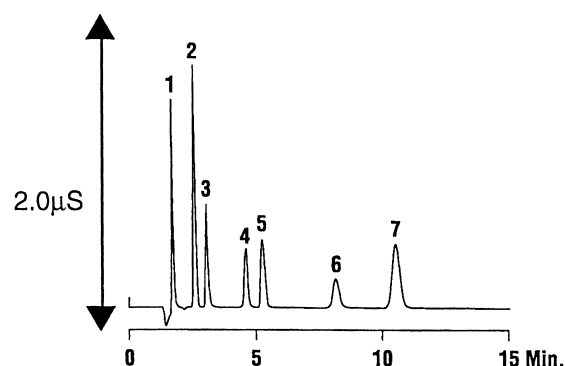
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Fig. 1. Common anions and disinfection byproducts (EPA method 300.1, Part B), (a) with DS-Plus suppressor; (b) with ASRS suppressor, recycle mode. Peak identification: 1, fluoride (1 mg/l); 2, chlorite (0.5 mg/l); 3, bromate (0.05 mg/l); 4, chloride (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,  $250 \times 4.0$  mm; mobile phase:  $9.0 \text{ mM Na}_2\text{CO}_3$ ; flow-rate: 1.0 ml/min; detection: suppressed conductivity; injection volume: 200  $\mu\text{l}$ .

gram was obtained using a membrane suppressor, the large water dip interferes with the fluoride peak. The DS-Plus suppressor gives no water dip with a



a



b

Fig. 2. Inorganic anions, (a) with DS-Plus suppressor; (b) with ASRS suppressor, recycle mode. Peak identification: 1, fluoride (2 mg/l); 2, chloride (4 mg/l); 3, nitrite (4 mg/l); 4, bromide (4 mg/l); 5, nitrate (4 mg/l); 6, phosphate (6 mg/l); 7, sulfate (6 mg/l). Column: AS4A-SC,  $250 \times 4.0$  mm; mobile phase:  $1.7 \text{ mM NaHCO}_3/1.8 \text{ mM Na}_2\text{CO}_3$ ; flow-rate: 1.0 ml/min; detection: suppressed conductivity; injection volume: 100  $\mu\text{l}$ .

background of  $1 \mu\text{S}$  compared to the water dip from Dionex ASRS suppressor with a background of  $15 \mu\text{S}$ . A calibration curve for fluoride was constructed with standards of 0.2, 2, 20, and 200  $\mu\text{g/l}$ . The standards were analyzed with a Novosep A-1 column and a mobile phase of  $1.7 \text{ mM NaHCO}_3/1.8 \text{ mM Na}_2\text{CO}_3$ . The method was optimized using the Dionex ASRS (external water mode) and then run on the DS-Plus suppressor. The calibration curves from the suppressors gave the following correlation coefficients: the DS-Plus suppressor has an  $R^2$ -value of 0.9999 compared to an  $R^2$  value of 0.9984 for the Dionex ASRS. Reduced water dip and improved

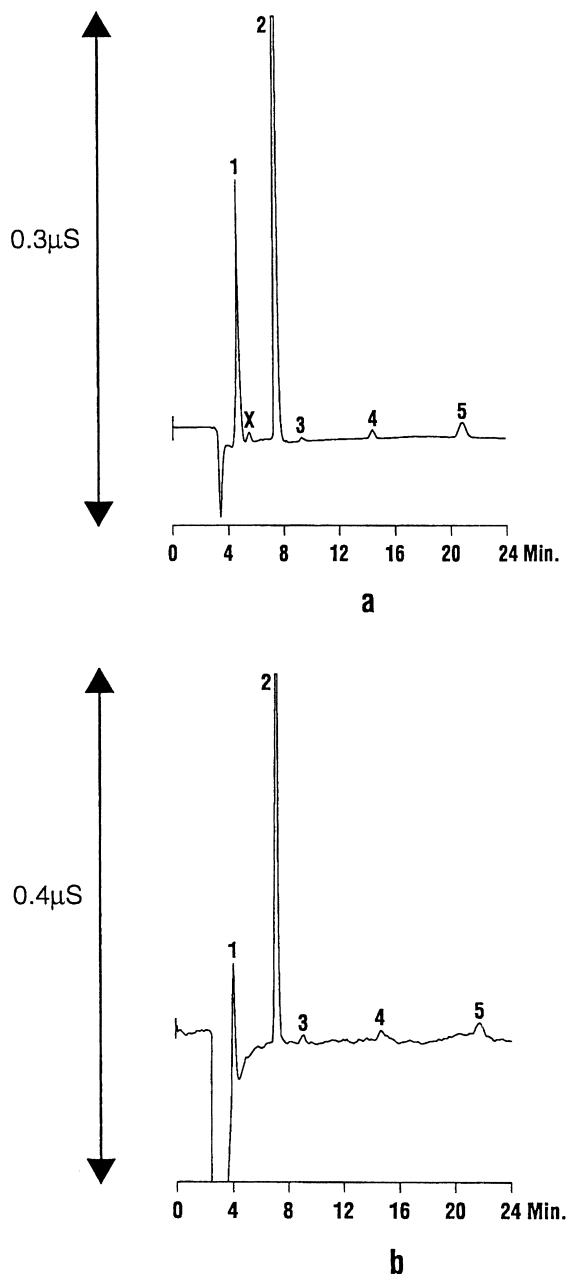


Fig. 3. Trace anions in water, (a) with DS-Plus suppressor; (b) with ASRS suppressor, external water mode. Peak identification: 1, fluoride (83  $\mu\text{g/l}$ ); 2, chloride (210  $\mu\text{g/l}$ ); 3, nitrite (3  $\mu\text{g/l}$ ); 4, nitrate (12  $\mu\text{g/l}$ ); 5, sulfate (16  $\mu\text{g/l}$ ); 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  $\mu\text{l}$ .

signal-to-noise ratio leads to more confident quantification of trace fluoride.

The removal of the dissolved carbon dioxide from the suppressor effluent [7] also improves the signal-to-noise ratio, increasing detection sensitivity. It is possible to detect analytes in the low  $\mu\text{g/l}$  to high  $\text{ng/l}$  range with the DS-Plus suppressor, without the need for preconcentration. Fig. 3 is a comparison of trace anions in water with the Dionex ASRS (external water mode) and the DS-Plus suppressor. The DS-Plus suppressor has a much smoother and more stable baseline with less water dip interference than the ASRS suppressor. Trace anions in morpholine are shown in Fig. 4. The DS-Plus suppressor easily detects 600  $\text{ng/l}$  fluoride while the Dionex ASRS

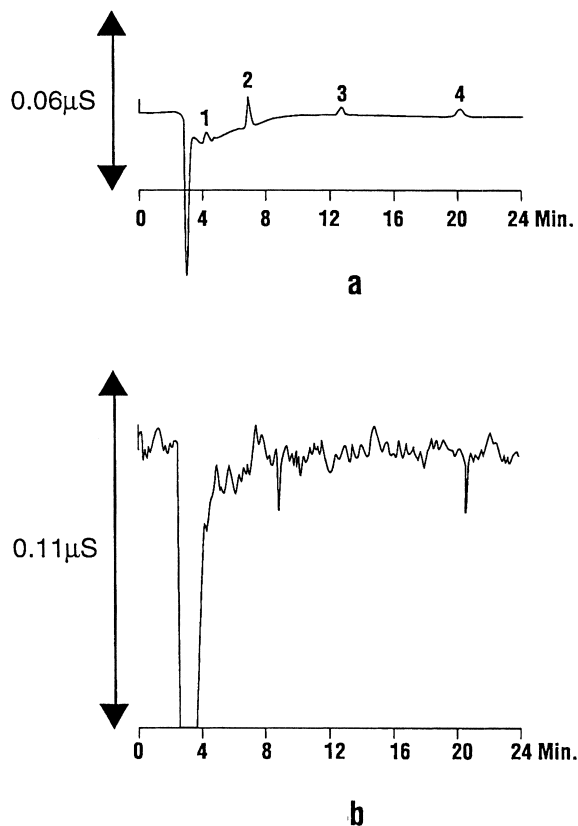


Fig. 4. Trace anions in morpholine, (a) with DS-Plus suppressor; (b) with ASRS suppressor, external water mode. Peak identification: 1, fluoride (0.6  $\mu\text{g/l}$ ); 2, chloride (5  $\mu\text{g/l}$ ); 3, nitrate (3  $\mu\text{g/l}$ ); 4, sulfate (2  $\mu\text{g/l}$ ). Column: AS9-HC, 250 $\times$ 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  $\mu\text{l}$ .

(external water mode) gives no identifiable peaks, only baseline noise. Even though 200  $\mu\text{l}$  is the highest sample volume used in this study, a higher injection volume may be used to increase the detection sensitivity.

This increased sensitivity lowers the method detection limits. Table 1 summarizes the method detection limits (MDLs) for EPA method 300.1 with the DS-Plus suppressor and the published MDLs of the EPA [10]. The values reported by the EPA were obtained with a 2 mm I.D. Dionex AS9-HC column and the narrow-bore method. The values of the 2 mm column are claimed to be a  $4\times$  improvement over the 4 mm column and the large-bore method [4]. We used a Dionex AS9-HC,  $250\times 4.0$  mm column with the DS-Plus suppressor and calculated the MDL values using the same procedure as that in method 300.1. To compensate for the  $4\times$  increase in the cross-sectional area of the column, the injection volume was increased  $4\times$  [10]. These MDLs show a large improvement over the values published in 300.1. The improved signal-to-noise ratio with the DS-Plus suppressor lowers the MDL of the method.

Table 1  
Method detection limit for EPA method 300.1, part A

Ion	EPA 300.1 [10] ( $\mu\text{g/l}$ )	With DS-Plus suppressor ( $\mu\text{g/l}$ )
Fluoride	9	0.3
Chloride	4	0.6
Nitrite-N	1	0.9
Bromide	14	2.8
Nitrate-N	8	0.4
Orthophosphate-P	19	1.4
Sulfate	19	1.2

#### 4. Conclusion

The new technology introduced in the Alltech DS-Plus suppressor improved results for trace level anion analysis. The degassing feature lowers the background conductance of sodium carbonate–sodium hydrogencarbonate mobile phases, improving baseline stability and detection limits. The water-dip often seen with conventional suppressors is greatly reduced, improving fluoride quantification.

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