

# New suppressor technology improves the ion chromatographic determination of inorganic anions and disinfection by-products in drinking water

Rakesh Bose<sup>a,\*</sup>, Raaidah Saari-Nordhaus<sup>a</sup>, Adesola Sonaike<sup>b</sup>, Dhanwant S. Sethi<sup>b</sup>

<sup>a</sup> Alltech Associates Inc., 2051 Waukegan Road, Deerfield, IL 60015, USA

<sup>b</sup> EnviroAnalytical Inc., 627 Main Street, Monroe, CT 06468, USA

Available online 17 March 2004

## Abstract

This paper describes a new suppressor technology for analyzing water samples using United States Environmental Protection Agency (EPA) methods 300.0 and 300.1. The Alltech DS-Plus suppressor improves and simplifies anion analysis in drinking water. In addition to suppressing the carbonate mobile phase and enhancing the analyte signal like conventional ion chromatography (IC) suppressors, the DS-Plus suppressor removes carbonic acid (as dissolved carbon dioxide) from the suppressor effluent before detection (US patent Nos.: 6 444 475; 6 468 804; others pending), lowering the background conductivity to near zero. Anions are detected in water background, improving sensitivity and lowering detection limits. The water-dip often seen with conventional suppressors is greatly reduced, improving fluoride quantification. The DS-Plus suppressor operates continuously without the need for external regenerants or switching valves. The performance of this new suppressor for analyzing water samples has been found to meet the EPA methods specifications.

© 2004 Elsevier B.V. All rights reserved.

**Keywords:** Disinfection by-products; Water analysis; Oxyhalides; Inorganic anions

## 1. Introduction

The key to increased human productivity and long life is good quality water [1]. Most people drink tap water that meets all existing health standards all the time. Water at a municipal treatment plant is made free of microorganisms by killing them with oxidizing chemicals. While disinfectants are effective in controlling many microorganisms, they react with natural organic and inorganic matter in source water and distribution systems to form organic (trihalomethanes and haloacetic acids) and inorganic oxyhalide byproducts known as “inorganic disinfection byproducts” (IDBPs) [2]. Many of the IDBPs have been shown to cause cancer and reproductive and developmental defects in laboratory animals. They are harmful to humans and are suspected carcinogens even at low parts per billion (ppb) levels. Under the United States Environmental Protection Agency (EPA) Information Collection Rule (ICR), utilities that use hypochlorite solution as a disinfectant are required to monitor chlorate. Utili-

ties using chlorine dioxide are required to monitor chlorite, chlorate, and bromate. If using ozone, utilities are required to monitor bromate.

The EPA has published several authoritative regulatory methods to provide mandatory procedures for IDBPs in drinking water [3]. Large surface water systems are required to comply with the Stage 1 Disinfectants and Disinfection Byproducts Rule and Interim Enhanced Surface Water Treatment Rule. Ground water systems and small surface water systems must comply with the Stage 1 Disinfectants and Disinfection Byproducts Rule by January 2004. The Stage 1 Disinfectant and Disinfection Byproduct Rule updates will also help to reduce exposure to disinfectants and many IDBPs. The rule establishes maximum contaminant level goals (MCLGs) and maximum contaminant levels (MCLs) for chemicals including chlorite and bromate. These new rules will further strengthen the existing drinking water standards and thus increase protection for many water systems.

IC is widely used for monitoring inorganic ions. In fact, IC with chemically suppressed conductivity detection is the only practical method for the monitoring and differentiation of IDBPs [4]. The EPA methods 300.0 and 300.1 use a

\* Corresponding author. Fax: +1-8479481078.

E-mail address: [rbose@alltechemail.com](mailto:rbose@alltechemail.com) (R. Bose).

sodium carbonate mobile phase, a column that separates the seven common anions and oxyhalides, a suppressor, and a conductivity detector. Several methods have been published to improve the limits of detection for the inorganic anions and the DBPs [5–7]. Advances in column resins, instrumentation, and even various modes of detection have improved the analysis of ions at trace levels. Advancement in ion chromatography suppressor has also been shown to improve and simplify IC separation and detection [8,9]. This paper discusses the application of this new suppressor for the determination of inorganic anions and IDBPs in reagent water, surface, ground water, and drinking water.

## 2. Experimental

The chromatography system consisted of a Model L-7100 HPLC pump (Hitachi, Tokyo, Japan), a Model 570 Autosampler, a Model 530 column heater, a DS-Plus suppressor, a Model 335 suppressor module, and a Model 650 conductivity detector, all from Alltech Associates (Deerfield, IL, USA). A Waters (Milford, MA, USA) Model 430 conductivity detector, a Milton Roy (Ivylnd, PA, USA) Model CM 4000 HPLC pump, and a Model ISS-100PE (Perkin-Elmer Instruments, Shelton, USA) autosampler with polyether ether ketone (PEEK) sample loops were also used. Alltech's Novosep A-2 Anion column (250 mm × 4.0 mm) was used for separations. The Dionex (Sunnyvale, CA, USA) ASRS membrane suppressor and IonPac AS9-HC (250 mm × 4.0 mm) column were also used. The Alltech Allchrom data system and the Agilent (Palo Alto, CA, USA) HP Chemstation data system were used to obtain the chromatograms.

Anion standards were prepared by dilution of 200 mg/l certified IC standards from Alltech. The mobile phase buffer was prepared using the Alltech's EZ-LUTE buffer concentrates. Deionized water was obtained from Milli-Q (Millipore, Bedford, MA, USA) equipment with a conductivity of 0.054  $\mu\text{S}/\text{cm}$ , and was used for preparing all solutions. The water samples were filtered through a 0.2  $\mu\text{m}$  Anotop IC syringe filter (Alltech) before injection.

## 3. Results and discussions

### 3.1. Advantages of the DS-Plus suppressor

Two types of suppressors are used in this study. The DS-Plus suppressor is the new suppressor that improves and simplifies anion analysis [8]. It is a packed bed suppressor that operates continuously without the need for any external regenerant or reagent. 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-hydrogen carbonate mobile phases are used) before it enters the conductivity detector. This patented

degassing process removes dissolved carbon dioxide ( $\text{CO}_2$ ) from the suppressor effluent, lowering the background conductivity. The drop in the background conductivity minimizes the water dip that often interferes with early eluting peaks and improves the detection sensitivity [9]. Another suppressor used in this study is the model 335 suppressor. It is a solid-phase chemical suppressor (SPCS) that uses disposable packed-bed cartridges as the suppression device [10]. Since the cartridges are discarded when exhausted, no regeneration reagent or equipment is required. Each cartridge lasts between 4 and 16 h depending on applications. For this EPA application, the cartridge lasted about 4.5 h. Fully unattended or overnight operation is not possible. Such a suppressor does not remove dissolved  $\text{CO}_2$  as discussed earlier and the results obtained with this suppressor in term of water dip and detection sensitivity are similar to other conventional suppressors that do not use the degassing process.

Fig. 1 shows the separation of the 10 anions obtained using the DS-Plus suppressor (Fig. 1a) and the 335 suppressor (Fig. 1b). Greater sensitivity is achieved with the DS-Plus suppressor for the same analyte concentrations and the size of the water dip is significantly reduced. The advantages of the smaller water dip using the DS-Plus suppressor can clearly be seen when a lower capacity column is used. Fig. 2 shows the separation of the 10 anions using the AS9-HC

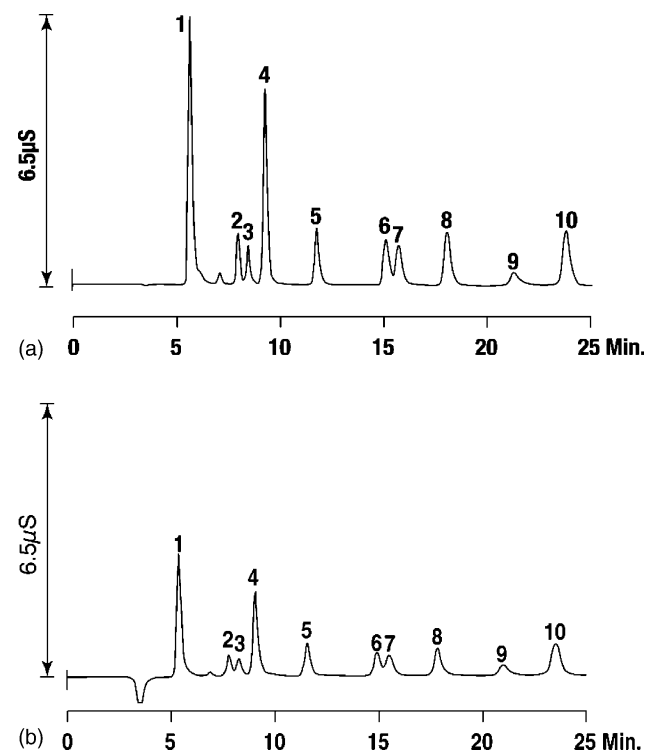


Fig. 1. Separation of common anions and oxyhalides with (a) DS-Plus suppressor and (b) SPCS suppressor : (2 mg/l of each) (1) fluoride; (2) chlorite; (3) bromate; (4) chloride; (5) nitrite-N; (6) bromide; (7) chlorate; (8) nitrate-N; (9) phosphate-P; (10) sulfate. Column: Novosep A-2, 250 mm × 4.0 mm; mobile phase: 3.6 mM sodium carbonate; flowrate: 0.8 ml/min; detection: suppressed conductivity; injection volume: 100  $\mu\text{l}$ .

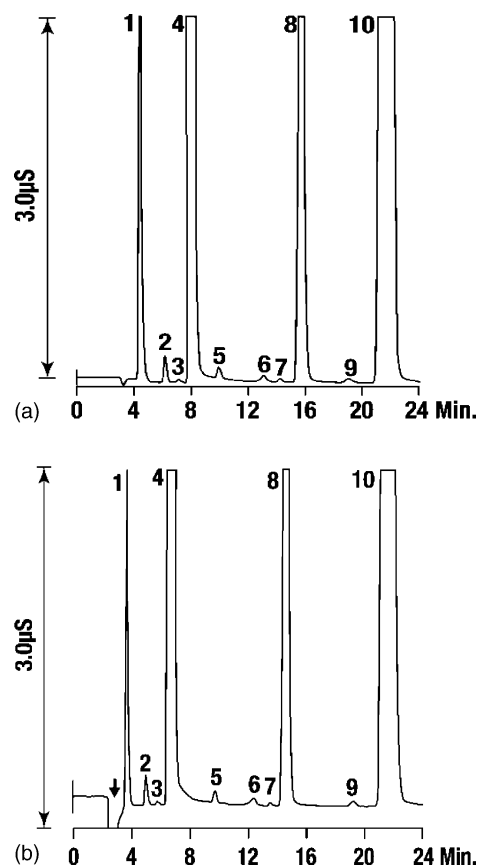


Fig. 2. Separation of common anions and oxyhalides with (a) DS-Plus suppressor and (b) ASRS membrane suppressor: (1) fluoride (1 mg/l); (2) chlorite (0.5 mg/l); (3) bromate (0.05 mg/l); (4) chloride (50 mg/l); (5) nitrite-N (0.1 mg/l); (6) bromide (0.05 mg/l); (7) chlorate (0.05 mg/l); (8) nitrate-N (10 mg/l); (9) phosphate-P (0.1 mg/l); (10) sulfate (50 mg/l). Column: IonPac AS9-HC, 250 mm  $\times$  4.0 mm; mobile phase: 9.0 mM sodium carbonate; flowrate: 1.0 ml/min; detection: suppressed conductivity; injection volume: 200  $\mu$ l.

column. This was the column used in the EPA study for method 300.1. In Fig. 2a, when the column is used with the DS-Plus suppressor, the background conductivity is reduced to 1  $\mu$ S and the fluoride peak is fully resolved from the water dip, even with this 200  $\mu$ l injection. With the suppressor that does not remove the dissolved CO<sub>2</sub> from the suppressor effluent, the water dip interferes with fluoride peak as shown in Fig. 2b. Without the CO<sub>2</sub> removal, the background conductivity is approximately 15  $\mu$ S.

### 3.2. Separation with the EPA methods

Fig. 3 shows the separation of the common anions, oxyhalides, and the surrogate dichloroacetic acid using a Novosep A-2 column. The capacity of this column is slightly higher than the column specified in the EPA method. This can be an advantage especially when larger injection volume is used to decrease the method detection limits (MDLs). Fig. 4 shows the separation of trace level oxyhalides along with other anions in simulated high ionic

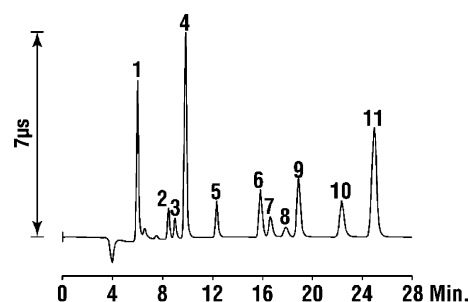


Fig. 3. Separation of common anions and oxyhalides with DS-Plus suppressor: (2 mg/l of each) (1) fluoride; (2) chlorite; (3) bromate; (4) chloride; (5) nitrite-N; (6) bromide; (7) chlorate; (8) dichloroacetate; (9) nitrate-N; (10) phosphate-P; (11) sulfate. Column: Novosep A-2, 250 mm  $\times$  4.0 mm; mobile phase: 3.6 mM sodium carbonate; flowrate: 0.8 ml/min; detection: suppressed conductivity; injection volume: 100  $\mu$ l.

strength drinking water. Good resolution is achieved for bromate in the presence of high chloride (100 mg/l) concentration. In addition to resolving fluoride from the water dip, such a high capacity column also improves the resolution between all the anions and in some cases eliminates the need for sample pretreatment.

Fig. 5a and b show the chromatograms of utility water samples using EPA methods 300.1 parts A and B, respectively. All anions are well resolved and can be accurately quantified.

### 3.3. Method detection limits, linearity, and recovery

Tables 1 and 2 summarize the retention time and the method detection limits of common anions and oxyhalides for EPA method 300.1 obtained using the Novosep A-2 column and the DS-Plus suppressor. The increased sensitivity as a result of the CO<sub>2</sub> removal from the detector effluent lowers the overall MDLs in comparison to the published MDLs in the EPA method [5]. Our MDL values are based on 200  $\mu$ l sample injections.

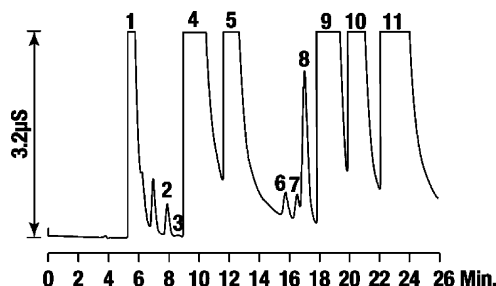


Fig. 4. Trace levels of oxyhalides and bromide in simulated high ionic strength drinking water using DS-Plus suppressor: (1) fluoride (1 mg/l); (2) chlorite (0.1 mg/l); (3) bromate (0.005 mg/l); (4) chloride (100 mg/l); (5) nitrite-N (10 mg/l); (6) bromide (0.020 mg/l); (7) chlorate (0.100 mg/l); (8) dichloroacetate (1 mg/l); (9) nitrate-N (10 mg/l); (10) phosphate-P (10 mg/l); (11) sulfate (100 mg/l). Column: Novosep A-2, 250 mm  $\times$  4.0 mm; mobile phase: 3.6 mM sodium carbonate; flowrate: 0.8 ml/min; detection: suppressed conductivity; injection volume: 100  $\mu$ l.

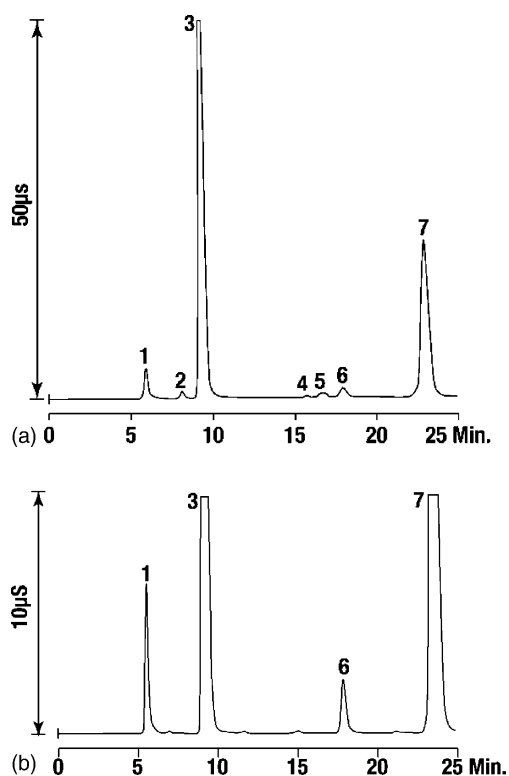


Fig. 5. Analysis of (a) utility water A and (b) utility water B with EPA method using DS-Plus suppressor: (1) fluoride; (2) chlorite; (3) chloride; (4) chlorate; (5) surrogate (DCA); (6) nitrate; (7) sulfate. Column: Novosep A-2, 250 mm  $\times$  4.0 mm; mobile phase: 3.6 mM sodium carbonate; flowrate: 0.8 ml/min; detection: suppressed conductivity; injection volume: 100  $\mu\text{l}$ .

A series of chlorite, bromate, and chlorate anions in the concentration range of 50 and 1000  $\mu\text{g/l}$  were injected along with dichloroacetate (DCA) as the surrogate. The peak areas were plotted against the concentrations. Table 3 summarizes

Table 1  
MDL for inorganic anions in reagent water

	$t_R$ (min)	Fortified concentration (mg/l)	MDL (mg/l)
Fluoride	6.27	0.02	0.001
Chloride	9.42	0.02	0.001
Nitrite-N	11.98	0.01	0.001
Bromide	15.5	0.04	0.004
Nitrate-N	18.5	0.01	0.005
Phosphate-P	21.85	0.04	0.007
Sulfate	24.09	0.04	0.001

MDL = S.D.  $\times$  3.14 for  $n = 7$ ; 3.6 mM sodium carbonate at 0.8 ml/min, 200  $\mu\text{l}$  loop.

Table 2  
MDL for oxyhalides in reagent water

	$t_R$ (min)	Fortified concentration ( $\mu\text{g/l}$ )	MDL ( $\mu\text{g/l}$ )
Chlorite	8.14	2	1.36
Bromate	8.76	2	0.59
Bromide	15.55	2	0.92
Chlorate	16.51	2	0.22

MDL = S.D.  $\times$  3.14 for  $n = 7$ ; 3.6 mM sodium carbonate at 0.8 ml/min, 200  $\mu\text{l}$  loop.

Table 3  
Linearity concentration range for oxyhalides in reagent water

	$t_R$ (min)	Concentration ( $\mu\text{g/l}$ )	S.D. ( $\mu\text{g/l}$ )	$r^2$
Chlorite	8.16	50–1000	49.67	0.999
Bromate	8.68	50–1000	51.60	0.997
Chlorate	15.82	50–1000	67.28	0.999
DCA Surrogate	16.69	1 ppm		

Table 4  
Recovery data for surrogate in reagent water

	Standard 1 (mg/l)	Standard 2 (mg/l)	Standard 3 (mg/l)	Standard 4 (mg/l)
Chlorite	0.049	0.099	0.493	0.986
Bromate	0.050	0.101	0.503	1.006
Chlorate	0.050	0.100	0.500	1.000
DCA surrogate (%)	99.40	103	103	100

Table 5  
Recovery data for oxyhalides in drinking water

	Percentage value	Fortified concentration (mg/l)
Chlorite	121	0.493
Bromate	118	0.503
Chlorate	118	0.500
DCA surrogate <sup>a</sup>	118–121	

<sup>a</sup> Sample also contained chloride (5–20 mg/l) and nitrate (0.1–1.0 mg/l).

the correlation coefficient values, which are near unity, indicating good system ruggedness and column performance.

Recovery data for the surrogate ion and oxyhalides from replicate analysis of fortified samples were obtained in drinking water and reagent water. Table 4 shows the recovery data for the surrogate ion in four standards within the concentration range of 50–1000  $\mu\text{g/l}$ . The recovery values were 99.4, 103, 103, and 100%. For the drinking water samples containing chloride and nitrate between the concentrations of 5–20 mg/l and 0.1–1.0 mg/l, respectively, the surrogate recoveries were 118–121% as listed in Table 5. The recovery values for the oxyhalides were also between 118 and 121%. These values are within the recovery windows of the EPA methods.

#### 4. Conclusion

The DS-Plus suppressor improves and simplifies EPA methods 300.0 and 300.1. The removal of the carbonic acid from the suppressor effluent reduces the background conductivity, substantially improving the baseline stability and detection limits. The size of the water dip is greatly reduced, improving the quantification of early eluting peaks. Since the DS-Plus suppressor operates continuously, the system requires little maintenance and unattended operation is possible.

## References

- [1] E.T. Urbansky, M.L. Magnuson, *Anal. Chem.* 74 (2002) 261A.
- [2] D.P. Hautman, D.J. Munch, C. Frebis, H.P. Wagner, B.V. Pepich, *J. Chromatogr. A* 920 (2001) 221.
- [3] <http://www.epa.gov/safewater/methods/sourcalt.html>.
- [4] EPA Method 300.1, Determination of Inorganic Anions in Drinking Water by Ion Chromatography, US Environmental Protection Agency, Cincinnati, OH, 1997.
- [5] P.E. Jackson, K. Chassaniol, *J. Environ. Monit.* 4 (2002) 10.
- [6] D.P. Hautman, D.J. Munch, Method 300.1, Determination of Inorganic Anions in Drinking Water by Ion Chromatography, US Environmental Protection Agency, Cincinnati, OH, 1999.
- [7] Application Note 136, Determination of Inorganic Oxyhalide Disinfection Byproducts Anions and Bromide in Drinking Water Using Ion Chromatography with the Addition of a Postcolumn Reagent for Trace Bromate Analysis, Dionex, Sunnyvale, CA.
- [8] R. Saari-Nordhaus, J.M. Anderson Jr., *J. Chromatogr. A* 956 (2002) 15.
- [9] D.R. Douglas, R. Saari-Nordhaus, P. Despres, J.M. Anderson Jr., *J. Chromatogr. A* 956 (2002) 47.
- [10] R. Saari-Nordhaus, J.M. Anderson Jr., *Am. Lab.* 26 (1) (1994) 28C.