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Journal of Chromatography A, 956 (2002) 53–58

JOURNAL OF
CHROMATOGRAPHY A

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Ion chromatographic system with a novel switching suppression device

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Abstract

Ion chromatography (IC) has been a powerful tool for measuring ionic species in environmental samples such as tap, river and drain waters. Suppressor modules (membrane and disposable column types) have been used for reducing the background of a baseline. A new type of suppressor device, which has a suppressor resin and switching valve was developed. Fresh ionic resin is introduced into a groove for each analysis to perform the suppression of the working eluent. The eluent composition for obtaining higher sensitivity and better resolutions among ionic species and carbonate ion was also investigated. Although carbonate buffers are used for ion separation in general, the separation of carbonate ion from other ions was not achieved. A borate eluent resulted in good resolutions and higher sensitivity. A new column was also developed for obtaining higher column efficiency and resolution. The optimization of anion separation using a new IC system (IC-2001) that consists of a new suppressor device, an anion-exchange column (TSKgel SuperIC-Anion, 150×4.6 mm), an autosampler, a conductivity cell and a pump in a compact module is described. © 2002 Published by Elsevier Science B.V.

Keywords: Instrumentation; Ion chromatography; Suppressor; Switching valve; Inorganic anions

1. Introduction

Ion chromatography (IC) is a versatile and widely accepted technique for the analysis of inorganic and organic ions [1]. In IC, a “suppressor system” is commonly used for a sensitive detection of ions on the basis of their electrical conductance. Its function is to reduce chemically the background conductivity of the electrolyte of an eluent before it enters the conductivity cell [2].

Although various suppressor devices have been

developed for IC, membranes and solid-phase column are the most commonly used suppressors [1].

The solid-phase column suppressor was originally proposed by Small et al. [3]. Recently, disposable packed-bed cartridges are commercial available as a suppressor device [4]. It is more rugged than membrane suppressors. Since the inexpensive cartridges are discarded when exhausted, no regeneration or maintenance is required. This characteristic eliminates the need for regeneration or complex post-column reaction systems [5]. The packed bed suppressors often have some problems associated with band broadening, variable retention time, peak area and the oxidation of nitrites in the suppressor [6].

Today the membrane suppressor is commonly

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employed with IC in most of the analytical laboratories [7]. Two semi-permeable ion-exchange membranes sandwiched between three sets of screens are normally used. The eluent passes through a central chamber, which has ion-exchange membrane sheets as the upper and lower surfaces. Regenerant flows in a counter-current direction over the outer surfaces of both of these membranes providing a constant regeneration. The regeneration is carried out either by passing a constant flow of a regenerant solution from an outside source, or by the water electrolysis or detector effluent to produce hydrogen or hydroxide ions required for regeneration [8].

The membrane suppressors that require a constant flow of regenerant from outside source have several drawbacks. These can consume large volumes of regenerant solution and therefore, produce large volumes of chemical waste. An additional pumping device is also required to continuously pass the regenerant through the suppressor, increasing the instrument's complexity and cost while reducing reliability. Chemical reactions that form precipitates may also irreversibly damage the membranes. In addition, organic compounds in samples could irreversibly adsorb onto the hydrophobic ion-exchange membrane resulting in reducing its efficiency to the point where it could require replacement [9].

The improvement and simplification of an IC system by using a new switching suppression device is comprehensively discussed in this paper.

2. Experimental

2.1. Instrumentation

IC was performed on a Model IC-2001 equipped with the following devices: a vacuum degasser, a pump, a column oven, an autosampler, a conductivity detector and a suppressor (Tosoh, Tokyo, Japan). Ion separation was carried out using a TSKgel SuperIC-Anion (150×4.6 mm, Tosoh) analytical column with a TSKguardcolumn SuperIC-A (10×4.6 mm, Tosoh) guard column. The experimental conditions for IC were as follows: a sample volume of 30 μ l, a flow-rate of 0.8 ml/min; and a column temperature of 40 °C.

Anions were detected by suppressed conductivity

detection in the IC-2001 system. For an experimental comparison the membrane suppressor (ASRS-ULTRA, Dionex, Sunnyvale, CA, USA) was also used and operated at 50 mA in the external water mode. Finally, an interface Model IC-WS (Tosoh) was used as a system controller and for processing the chromatographic data.

2.2. Reagents

Eluents, washing solvents and standard solutions were prepared with deionized water by Milli-Q equipment (Nippon Millipore, Tokyo, Japan).

All reagents of guaranteed reagent grade were purchased from Wako (Osaka, Japan).

The anion standard solution and multi-anion standard solution 1 (Wako) were diluted with the Milli-Q water for calibration purposes.

The cation-exchange resin (TSKsuppress IC-A from Tosoh, 200 μ m diameter, 1.7 mequiv./l) was used for improving the suppression process.

2.3. Procedure of suppression

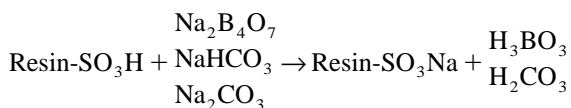
A summarized description of the suppression process is schematically presented in Fig. 1.

The suppressor valve consists of a six-port electronic rotary valve equipped with three grooves for packing the resin. Since the suppressor valve is switched in each injection, a new filled resin is always used for suppression in analyzing each sample. While the first groove (a) is used for measuring a sample, the resin used is discharged to drain from the second groove (b). At the same time, a fresh resin is filled into the third groove (c) to measure the next sample.

The filling and discharging of the resin and the washing of the groove is performed by water pressure using a syringe pump.

The resin that is used in the groove is strong a cation exchanger, so the chemical reaction in the suppressor valve (groove c) is the same as in original solid-phase column suppressor [1].

The chemical reaction is as follows:



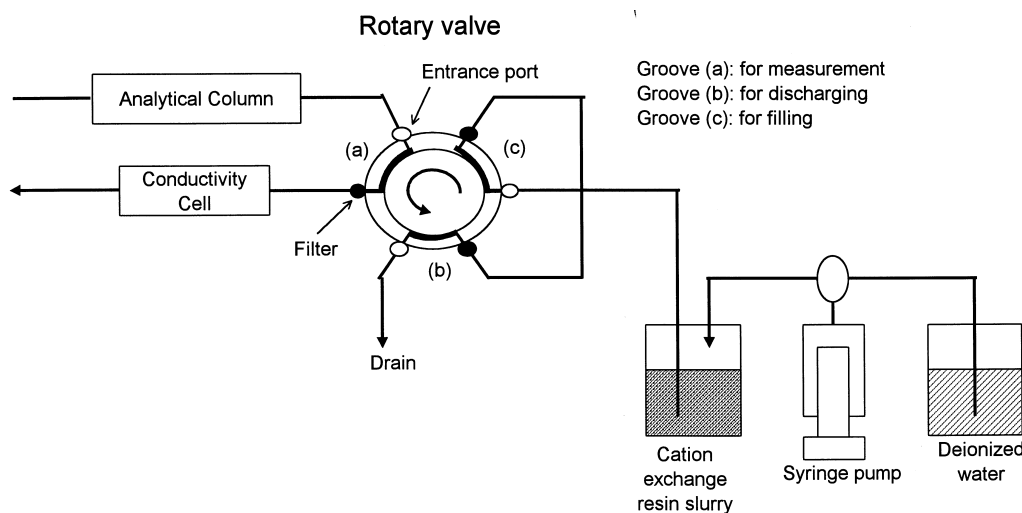


Fig. 1. The suppressor valve configuration in the IC-2001. The details are described in the text.

Since the resin for suppression in the groove is disposable, no regeneration of suppressor is required, and by-products and matrix in the samples do not damage the suppressor valve.

The small groove volume (200 μl) in the suppressor valve allows one to eliminate band broadening but has enough volume to measure one sample.

3. Results and discussion

3.1. Comparison with a membrane type suppressor

In order to compare the working efficiency of

membrane and switching valve suppressors, the theoretical plates and asymmetry factors were calculated. Such efficiency parameters were obtained from standard anion chromatograms using both membrane and switching valve suppressors (Table 1).

As can be seen, the membrane type suppressor provided lower theoretical plates and tailing factors than those related to the switching valve type suppressor, especially being remarkable for the anions eluted earlier such as fluoride and chloride.

The difference of void volume in a suppressor may cause band broadening on each peak shape. As it is necessary to enlarge the surface area of the membrane for the high capacity of continuous sup-

Table 1
Comparison chromatographic data using each suppressor

Anion	Switching valve type		Membrane type	
	Theoretical plates	Asymmetry factor	Theoretical plates	Asymmetry factor
Fluoride	9329	1.04	6294	1.85
Chloride	11 455	1.01	9749	1.27
Nitrite	9574	0.76	8687	0.94
Bromide	11 453	0.97	10 315	1.09
Nitrate	11 849	1.28	10 475	1.34
Phosphate	13 097	0.83	11 799	0.93
Sulfate	13 552	0.80	12 433	0.85

Eluent: 1.7 mM NaHCO_3 –1.8 mM Na_2CO_3 . Detection: suppressed conductivity with the suppressor valve. Peaks (mg/l): 1=water dip, 2=fluoride (1), 3=chloride (1), 4=carbonate dip, 5=nitrite (5), 6=bromide (5), 7=nitrate (5), 8=phosphate (10), 9=sulfate (5). Other chromatographic conditions as described in the text.

pression, the void volume is consequently large in the membrane type.

On the other hand, since a small volume of resin is required to measure one sample, the groove volume in the suppressor valve can be lowered (200 μl). Thus, the switching valve suppressor eliminates the band broadening problem due to the use of a small void volume.

3.2. Influence of mobile phase conditions

Borate and carbonate eluents were separately investigated for evaluating the efficient separation of anions on the TSKgel SuperIC-Anion column. Fig. 2 presents ionic chromatograms showing the anion separation of a standard mixture sample.

While the carbonate ion is converted to the carbonic acid as its conjugate acid, the borate ion is converted to the boric acid, which has the lower dissociation constant ($\text{p}K_{\text{a}1}$ 9.24, at 25 $^{\circ}\text{C}$) [10].

The background conductivities of the carbonate

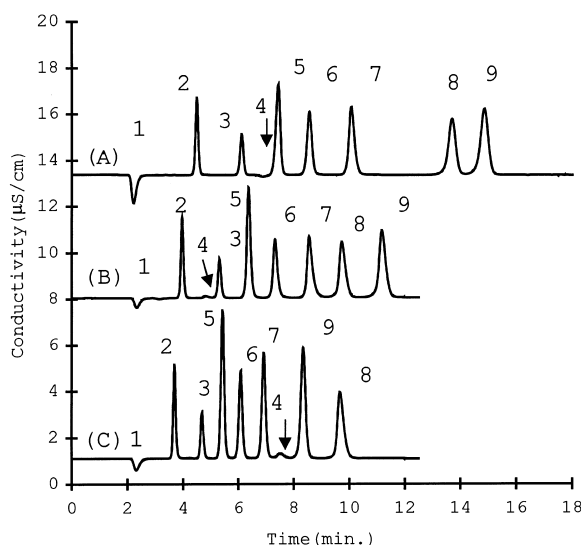


Fig. 2. Chromatogram of standard anions using the switching valve suppressor. Conditions: eluent: (A) 1.7 mM NaHCO_3 –1.8 mM Na_2CO_3 , (B) 6.0 mM $\text{Na}_2\text{B}_4\text{O}_7$ –15 mM H_3BO_3 –0.2 mM NaHCO_3 , (C) 1.2 mM $\text{Na}_2\text{B}_4\text{O}_7$ –0.2 mM Na_2CO_3 –6.5 mM NaOH , column: TSKgel SuperIC-Anion (150 \times 4.6 mm), flow-rate: 0.8 ml/min, column temperature: 40 $^{\circ}\text{C}$, detection: suppressed conductivity, injection volume: 30 μl . Peaks (mg/l): 1=water dip; 2=fluoride (1); 3=chloride (1); 4=carbonate dip; 5=nitrite (5); 6=bromide (5); 7=nitrate (5); 8=sulfate (5); 9=phosphate (10).

and borate eluents after suppression were ca. 16 and 8 $\mu\text{S}/\text{cm}$, respectively. In addition, the low detection noise obtained with the borate buffer leads to an improvement in the detection sensitivity of anions. Another advantage of measuring under lower background conductivity conditions was to decrease the water dip volume on the chromatogram.

The resolutions of fluoride ion and the water dip were remarkably improved, even if a trace amount of fluoride was small.

In general, one of the major problems in suppressed ion chromatography is to generate a carbonate dip on the chromatogram which interferes the determination of the remaining anionic species is used [11]. The carbonate dip is eluted with the chloride ion in many columns when a carbonate buffer is used.

Fig. 2 shows a comparison of the elution profile of anions when the carbonate (A) and borate buffers (B, C) are used. The use of carbonate eluent (A) caused an interference of a carbonate dip with the determination of nitrite ion.

On the other hand, the use of a borate eluent (C, pH 11.6) showed an excellent resolution among anions and the carbonate peak without any interference of the determination (Fig. 2C).

Another separation profile was obtained by using the borate buffer (pH 8.8). Under this condition, the carbonate dip was efficiently eluted before the chloride ion without any interference effect on the determination of the solute (Fig. 2B).

By choosing the composition of the eluent and pH, the elution volume of carbonate peak can be controlled for optimization.

3.3. Linearity, accuracy and detection limits

The linearity and detection limits data are summarized in Table 2. The calibration curves were evaluated by plotting peak area against the concentration of anions. The linear calibration curves were obtained in each concentration range. The coefficients of determination for anions ranged from 0.9951 to 0.9997.

The limits of detection (LODs) of each anion was defined as the detectable concentration of an anion giving a peak three-times as high as the background noise ($S/N=3$). These values were sufficiently low as the suppressed conductivity IC. Although the

Table 2
Calibration and detection limits data of standard anions using IC-2001

Anion	Concentration range of anion (mg/l)	Number of determinations	Coefficient of correlation (r^2)	Detection limit (S/N=3, $\mu\text{g/l}$)
Fluoride	0.005–20	10	0.9996	1.1
Chloride	0.005–20	10	0.9951	2.2
Nitrite	0.025–100	10	0.9996	4.1
Bromide	0.025–100	10	0.9966	8.5
Nitrate	0.025–100	10	0.9966	8.6
Phosphate	0.5–200	8	0.9973	16.4
Sulfate	0.025–100	10	0.9974	6.1

Eluent: 6.0 mM $\text{Na}_2\text{B}_4\text{O}_7$ –15 mM H_3BO_3 –0.2 mM NaHCO_3 . Detection: suppressed conductivity with the suppressor valve. Other chromatographic conditions as described in the text.

Three replicates of each.

Injection volume: 30 μl .

recovery of nitrite is often reduced by oxidation in the solid-phase suppressor, higher recovery of nitrite seems to be obtained in this system.

3.4. Reproducibility

The reproducibility of retention time and peak area is listed in Table 3 ($n=11$). The relative standard deviations (RSDs) of the retention time and peak area were less than 0.2 and 0.5%, respectively.

When using the conventional suppressor using a disposable packed-bed column, it is well-known that the decrease in retention time and detector response is observed due to the decrease in the cation-exchange capacity. However, a good reproducible chromatogram was obtained during the repeated chromatographic runs when using this novel suppression system.

3.5. Separation of real samples

The novel IC system developed here was applied to the analysis of anions in environmental samples such as tap and river water as shown in Fig. 3. Each

sample was analyzed after filtration through a 0.45- μm membrane filter.

A small amount of anions such as fluoride was detected from each sample solution with good resolutions.

Table 4 summarizes the determination and reproducibility of anions ($n=5$) in the environmental samples. It seems this IC system would be suitable for practical use.

For the evaluation of analytical results of practical samples determined by the proposed method, a detailed study is required and this will be the subject of future work.

4. Conclusion

In this study, the IC system (IC-2001) with a new type of suppressor device was described. Such a device has a suppressor resin and a switching valve.

Suppression was performed through the groove filled with cation-exchange resin in the suppressor valve.

The small groove (200 μl) is switched for every injection. This system provided an excellent repro-

Table 3
RSD data of analyzing standard anions ($n=11$)

	F	Cl	NO_2	Br	NO_3	PO_4	SO_4
Retention time (%)	0.082	0.046	0.054	0.049	0.045	0.028	0.044
Peak area (%)	0.41	0.48	0.41	0.41	0.43	0.53	0.41

Eluent: 6.0 mM $\text{Na}_2\text{B}_4\text{O}_7$ –15 mM H_3BO_3 –0.2 mM NaHCO_3 . Detection: suppressed conductivity with the suppressor valve. Other chromatographic conditions were described in the text. Sample concentration (mg/l): fluoride (1), chloride (1), nitrite (5), bromide (5), nitrate (5), phosphate (10), sulfate (5).

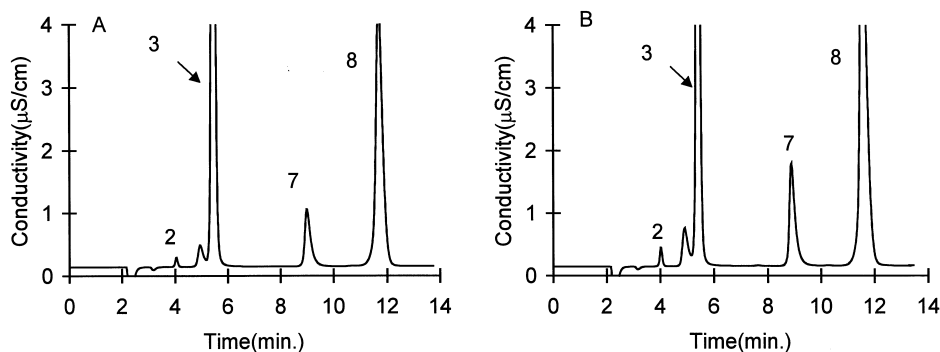


Fig. 3. Chromatograms of real samples. (A) Tap water, (B) river water. Eluent: 6.0 mM $\text{Na}_2\text{B}_4\text{O}_7$ –15 mM H_3BO_3 –0.2 mM NaHCO_3 . Detection: conductivity through the suppressor valve. Other chromatographic conditions were described in the text. Peaks: 2=fluoride, 3=chloride, 7=nitrate, 9=sulfate.

Table 4
Determination and reproducibility data of real samples

Anion	Tap water		River water	
	Determination (mg/l)	RSD (% , n = 5)	Determination (mg/l)	RSD (% , n = 5)
Fluoride	0.047	0.67	0.096	0.54
Chloride	8.92	0.33	6.98	0.64
Nitrate	1.64	0.45	3.22	0.58
Sulfate	5.79	0.38	8.75	0.47

Eluent: 6.0 mM $\text{Na}_2\text{B}_4\text{O}_7$ –15 mM H_3BO_3 –0.2 mM NaHCO_3 . Detection: suppressed conductivity with the suppressor valve. Other chromatographic conditions as described in the text.

ducibility and no decrease of column efficiency was observed due to the use of a fresh resin for each run and a reducing void volume.

The selection of borate buffer as a working eluent allowed a significant reduction of the interference problems caused by water dip and carbonate dip, as well as a higher detection sensitivity because of the low background conductivity.

The combination of this new suppressor, eluent and high-resolution column (TSKgel SuperIC-Anion) provides a simple, convenient, economical IC system and would be very useful in measurement of various ion species.

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