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Anion chromatography using on-line recycled eluents

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Abstract

Non-suppressed anion chromatography, using on-line recycled eluents, was investigated. Cations and anions from samples were excluded from the eluents using a mixture of strongly acidic cation-exchange resins and strongly basic anion exchange resins in the eluent reservoir. This exclusion was performed after determination of the anions in the non-suppressed anion chromatography, and the eluents were then recycled on-line. The performance of consecutive determinations was evaluated from the relative standard deviation (RSD) of peak heights and retention times of chloride, bromide, nitrite, nitrate, and sulfate ions, with a concentration of 3 μg ml^{-1} each, compared to that of normal anion chromatography. Over 50 consecutive determinations could be achieved with an eluent volume of only 200 ml for a 100 μl sample volume. Almost all the RSD values for retention time, and peak heights of these anions, were smaller than 3%. Over fifty consecutive determinations of chloride, nitrate, and sulfate ions in a river water sample could be achieved with an eluent volume of only 100 ml. All the RSD values for retention time and peak heights of these anions were smaller than 3%. The eluent volume could be decreased to one tenth of that used in normal anion chromatography. The performance of the anion chromatography, using on-line recycled eluents, was the same as that for normal anion chromatography under the same conditions.

Keywords: Non-suppressed anion chromatography; Inorganic anion; Recycled eluent; Consecutive determinations; Ion exchanger

1. Introduction

It is well known that ion chromatography (IC) is a useful tool for the determination of chloride, bromide, nitrite, nitrate, and sulfate ions in environmental and industrial waste samples [1–3]. However, a large volume of eluent is consumed in the measurement of many samples in normal IC. For example, when measuring these anions for 50 samples, using a flow rate of 1 ml min^{-1}, an eluent volume of 1000 ml is consumed. This is excluding the volume of eluent required to prepare calibration curves for the anions, and for stabilization of a background base-line, which is required because the retention time of the sulfate ion is normally ca. 20 min. Almost all the volume of this eluent is wasted, without any change to its chemical composition. Therefore, it would be highly advantageous to recycle the eluent. The generation and recycling of a potassium hydroxide eluent in suppressor type IC have been reported [4,5]. Identical chromatograms, between generation and recycling of the eluent, were obtained for approximately eight cycles in suppressor type IC, suggesting that the recycling of the eluent was successful. However, this includes disadvantages, such as the overheating of ion-exchange beds and the decomposition of nitrate ions, because of the use of electrically polarized ion-exchange beds.

Non-suppressor type IC has been well used, although not as well developed as suppressor type IC [3]. Non-suppressor type IC allows the convenient and easy change of eluent composition, when change of the selectivity for analyte ions is necessary, for a sample in a complex or difficult matrix. One Japanese standard determination method for these anions, using the non-suppressor type IC, requires the preparation of a complicated composition of eluent with low conductivity [6]. In order to measure a large number of samples, an analyst requires the preparation of either a large volume of eluent, or many smaller preparations of the eluent. Furthermore, once running of the IC system was stopped, re-stablization of background base-line associated with consuming the eluent

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would be requested for re-measurement. If the eluent could be recycled, the required number of tedious preparations of eluent could be decreased and the IC system could be continuously running for long terms without stopping it, even when it was not used. This has significant merit in the use of non-suppressor type IC. Recently, a recycling type of electrostatic ion chromatography (EIC) has been reported [7]. This recycling EIC has been achieved by the on-line re-coating of a zwitterionic surfactant on an ODS column, after separation of sample anions. Consequently, the recycling EIC had excellent reproducibility and longer run-time, better than the normal EIC. The recycling type EIC aims to regenerate the zwitterionic surfactant-coating ODS column on-line; however, a method to recycle and regenerate the eluent on-line has not been established in IC yet.

Some circular flow injection analysis (FIA) systems, used to recycle and regenerate reagent solutions on-line, have been reported [8,9]. The recycling FIA also has more excellent reproducibility and longer run-time than normal FIA. The important point is to regenerate and recycle the reagent solution on-line, so that if the principle of the recycling FIA, using a resin, was introduced into IC, the eluent could be recycled on-line. Furthermore, if the eluent volume was smaller than that used in normal IC, a newly developed type of IC would provide a great advantage to environmental chemistry. Accordingly, a circular non-suppressed anion chromatography system, that recycles the eluent on-line, was investigated.

2. Experimental

2.1. Reagents

A low-conductive eluent of 1.3 mM potassium gluconate, 1.3 mM sodium tetraborate, 30 mM boric acid, 100 $\mathrm{g\,l^{-1}}$ acetonitrile, and 5 $\mathrm{g\,l^{-1}}$ glycerol [6] was used. A strongly acidic cation exchange resin (Amberlite 200CT Na, Organo, Japan) and a strongly basic anion exchange resin (Amberlite IRA-900, ICN Biomedicals, USA) were procured for use in the regeneration of the eluent. 0.5 g of each of the cation and anion exchange resins were mixed and stirred three times in 500 ml of the low-conductive eluent for 30 min. The mixed ion exchange resins were free of chloride ions, which can contaminate the eluent. Also, the background base-line of the eluent, with the mixed ion resins added, could be kept constant over one day. Consequently, the mixed ion exchange resins were completely in equilibrium with the eluent. The mixed ion exchange resins after determination of the analyte ions could be also regenerated by the above method. The resins were used after filtration through an Advantec (Tokyo) No. 5C filter. All the sample solutions of inorganic anions were prepared from 100 $\mu\mathrm{g\,ml^{-1}}$ of sodium salt stock solutions, using reagent grade materials (Wako, Japan). Chloride, bromide, nitrite, nitrate, and sulfate ions, each at a concentration of 3 $\mu\mathrm{g\,ml^{-1}}$, were chosen as the anion samples, because these anions generally exist in the $\mu\mathrm{g\,ml^{-1}}$ range in natural waters of Japan. All water used was purified using Milli-Q water system (Millipore, Bedford, MA), after distillation through an ion exchange column. All solutions were filtered through a 0.45 μm mixed cellulose membrane (Advantec, Tokyo) before use.

2.2. Instrumentation

A non-suppressed anion chromatographic system was used, consisting of a Tosoh CCPD pump and CM 8000 conductivity detector, and a Rheodyne 7725 injector with a 100 μl sample loop. An anion exchange column (4.6 mm i.d. × 5 cm, Tosoh TSK-GEL IC-Anion-PW) was kept in an air-oven (Tosoh CO 8000) at a constant 30 °C. A flow rate of 1 $\mathrm{ml\,min^{-1}}$ was used for the anion exchange column.

3. Results and discussion

3.1. Mixed ion exchange resins in eluent

Fig. 1 shows a non-suppressed anion chromatographic system using on-line recycled eluents. One system puts the mixed cation and anion exchange resins into an eluent reservoir, in order to regenerate the eluent. The other was constructed without mixed ion exchange resins in the eluent reservoir. The eluent was continuously stirred during measurements, after replacing an old solution on the anion exchange column with a small volume of the eluent. The cation and anion exchange resins can exclude cations and anions in the injected sample on-line, respectively. Fig. 2 shows the dependency of the retention times and peak heights for chloride, bromide, nitrite, nitrate, and sulfate ions, on the number of successive samples injected into the anion chromatographic system, using the on-line recycled eluents without mixed ion exchange resins in the eluent. The peak heights of the chloride, bromide, nitrite, nitrate, and sulfate ions decreased after 15, 10, 19, 22, and 24 successive sample injections, respectively, for an eluent volume of 20 ml. The retention time of the sulfate ion gradually increased with increasing sample injection number for eluent volumes from 10 to 200 ml. The larger the eluent volumes were, from 10 to 200 ml, the smaller both the dependencies were, because the injected 100 μl sample solutions were diluted in a larger volume of eluent. When an eluent volume of 250 ml was used, both dependencies were very small, although a slight scatter in the plots was observed. Even a simple anion chromatographic system using on-line recycled eluents could achieve good reproducibility for the determination of all these anions for over 50 sample injections, using an eluent volume of 250 ml. The average and relative standard deviation (RSD) values of the peak heights and retention times with drifts of the retention times are summarized in Table 1. The drifts of retention times were calculated from equation: drift = (the last retention time − the first retention time)/injection number, since the retention times linearly increased with increasing

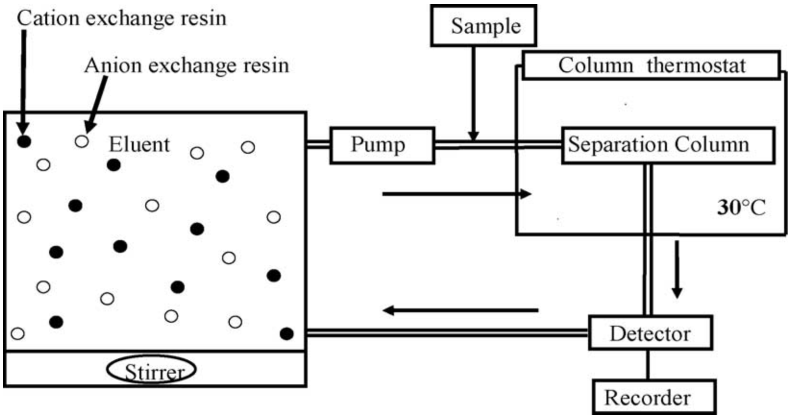

Fig. 1. Anion chromatographic system using on-line recycled eluents.

sample injections. The drifts of peak heights were not calculated, because the peak heights non-linearly decreased with increasing sample injections as shown in Fig. 2(b). In cases where the eluent volume was above 250 ml, almost all the RSD values were less than 3%. The RSD values were the same as those in normal IC (a flow-through IC) under the same conditions. If normal IC was used, an eluent volume over 1000 ml would be required for 50 injections, including stabilization of the base-line, because the measurement of one sample takes 20 min (The total effluent time for the sulfate ion was approximately 18 min in this IC system). The eluent volume required for the simple anion chromatographic system, using the on-line recycled eluents, could be one fourth less than that required in normal IC.

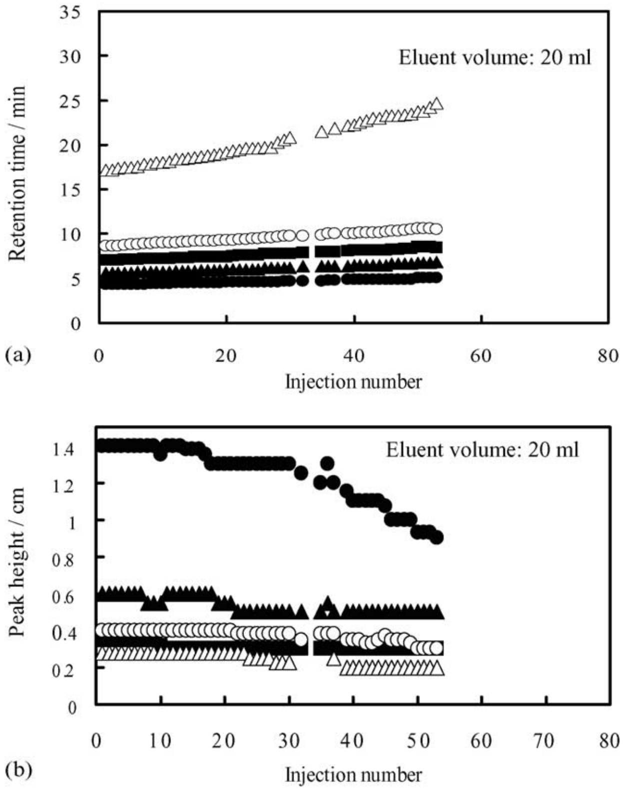

Fig. 2. Dependencies of retention times (a) and peak heights (b) for chloride, bromide, nitrite, nitrate, and sulfate ions, each at a concentration of 3 μg ml^{-1}, on the number of injections: closed circle, chloride; closed square, bromide; closed triangle, nitrite; open circle, nitrate; open triangle, sulfate.

The average and RSD values of the retention times and the peak heights of these anions for the 50 sample injections in the anion chromatography using on-line recycled eluents with the mixed ion exchange resins in the eluent, are summarized in Table 1. The peak heights of the chloride and nitrate ions were almost constant over 47 sample injections with an eluent volume of 20 ml, compared to those without the mixed ion exchange resins. The difference between the first and the last peak height of the chloride ion decreased from 0.47 without the resins to 0.05 cm with the resins. This shows that the mixed ion exchange resins eliminate the chloride ion from the eluent. The peak heights of the anions, except that of the sulfate ion, were constant for an eluent volume of 50 ml. The retention time of the chloride ion increased with increasing sample injection number for an eluent volume of 20 ml, although those of the other anions were almost constant. The peak heights and retention times of all the anions were almost constant over the 50 sample injections for an eluent volume of 200 ml. Fig. 3 shows dependencies of the retention times and peak heights of these anions on the number of sample injections in the anion chromatography, using on-line recycled eluents with the mixed ion exchange resins in the eluent. The eluent volume with the mixed ion exchange resins could be 50 ml less, compared to that without the mixed ion exchange resins. The eluent volume in the anion chromatographic system, using on-line recycled eluents, could be decreased to one fifth of that in normal IC. The performance of the anion chromatographic system using on-line recycled eluents in the determination of anions was the same as that of normal IC. This becomes a major advantage for environmental chemistry, due to the reduction in the amount of wasted eluent solution.

In this study, concentration of the analyte ions used was 3 μg ml^{-1} of each. If the concentration largely increased, the determination number would decrease. The dependency of

Table 1
Average and RSD values for retention times and peak heights of chloride, bromide, nitrite, nitrate, and sulfate ions after 50 injections with drifts of retention times

	Without resins[a]			With resins[a]		
	50[b]	100[b]	250[b]	20[b,c]	100[b,d]	200
Chloride ion						
Retention time/min (RSD, %)	4.02 (3.76)	3.81 (3.60)	3.93 (1.91)	4.36 (4.42)	4.13 (2.06)	3.81 (2.36)
Peak height/cm (RSD, %)	1.15 (1.50)	1.22 (2.06)	1.20 (0.99)	1.28 (1.95)	0.92 (2.72)	0.90 (0.00)
Drift of retention time/min injection^{-1}	0.0080	0.0050	0.0030	0.013	0.0051	0.0030
Nitrite ion						
Retention time/min (RSD, %)	5.02 (3.29)	4.80 (3.02)	4.94 (1.50)	5.60 (5.63)	5.26 (1.39)	4.80 (1.66)
Peak height/cm (RSD, %)	0.75 (6.25)	0.81 (2.11)	0.80 (0.00)	0.71 (12.3)	0.75 (6.60)	0.80 (0.00)
Drift of retention time/min injection^{-1}	0.010	0.0050	0.0030	0.022	0.0041	0.0030
Bromide ion						
Retention time/min (RSD, %)	6.17 (3.24)	5.90 (2.84)	6.08 (1.32)	7.00 (5.96)	6.47 (2.00)	5.92 (2.00)
Peak height/cm (RSD, %)	0.33 (9.98)	0.39 (3.95)	0.39 (3.21)	0.33 (14.2)	0.35 (14.5)	0.39 (4.22)
Drift of retention time/min injection^{-1}	0.013	0.0050	0.0050	0.028	0.0071	0
Nitrate ion						
Retention time/min (RSD, %)	7.40 (3.09)	7.04 (3.08)	7.29 (1.38)	8.57 (6.70)	7.70 (2.19)	7.10 (1.69)
Peak height/cm (RSD, %)	0.40 (3.49)	0.40 (1.08)	0.40 (0.00)	0.40 (0.00)	0.37 (6.76)	0.40 (0.00)
Drift of retention time/min injection^{-1}	0.015	0.0050	0.0080	0.038	0.010	0.0020
Sulfate ion						
Retention time/min (RSD, %)	16.03 (5.48)	14.67 (3.20)	14.74 (1.55)	18.48 (9.31)	16.96 (3.59)	15.08 (1.93)
Peak height/cm (RSD, %)	0.30 (0.96)	0.30 (0.00)	0.30 (0.00)	0.26 (17.2)	0.25 (19.1)	0.30 (0.00)
Drift of retention time/min injection^{-1}	0.055	0.024	0.017	0.12	0.044	0.019

[a] Condition.
[b] Eluent volume/ml.
[c] 47 injections.
[d] 49 injections.

the concentration on the determination number of the analyte ions was not investigated, because the concentration level was normally used in the determination of the analyte ions in IC (A sample of the large concentration was normally diluted to the concentration level). However, when the concentration largely increased, the mixed ion exchange resins weights used could be easily increased in this system.

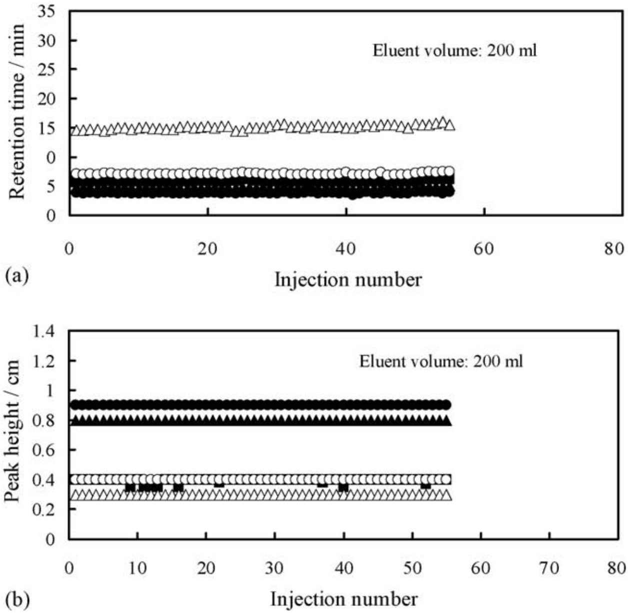

Fig. 3. Dependencies of retention times (a) and peak heights (b) for chloride, bromide, nitrite, nitrate, and sulfate ions, on the number of injections, with 1 g of the mixed ion exchange resins in the eluent. The symbol key is the same as that in Fig. 2.

3.2. Mixed ion exchange resins column after detector

It would be expected that a mixed ion exchange resin packed column would be more efficient for the regeneration and recycling of the eluent, rather than having mixed ion exchange resins added to the eluent reservoir [8]. The anion chromatographic system, using on-line recycled eluent equipped with the mixed ion exchange resins column between the conductivity detector and the eluent reservoir in Fig. 1, was investigated. Approximately 1 g of the mixed ion exchange resins were packed in a stainless steel column (4.6 mm i.d. × 25 cm), after being equilibrated in the eluent, as described in Section 2.

The background base-line increased with increasing number of sample injections, because the anions in the sample and the cations of those counter-ions were effused from the mixed ion exchange resins column by the eluent. This shows that the strongly acidic and basic mixed ion exchange resins could not fix the sample ions on the column. Although ion exchange equilibrium between the mixed ion exchange resins and almost all the eluent in a reservoir could be achieved in Section 3.1, the equilibrium between the resins and only a divisional eluent on the column could be achieved. Consequently, the anion chromatographic system, using on-line

Table 2
Average and RSD values for retention times and peak heights of ions in river water after 50 injections (eluent with mixed resins)

	Chloride ion		Nitrate ion		Sulfate ion	
Eluent volume/ml	50	100	50	100	50	100
Retention time/min (RSD, %)	3.82 (2.63)	3.79 (1.88)	6.83 (2.11)	6.82 (1.87)	14.32 (4.05)	13.97 (2.63)
Peak height/cm (RSD, %)	3.00 (2.11)	3.15 (2.11)	0.40 (1.77)	0.40 (1.06)	0.74 (5.63)	0.79 (2.33)

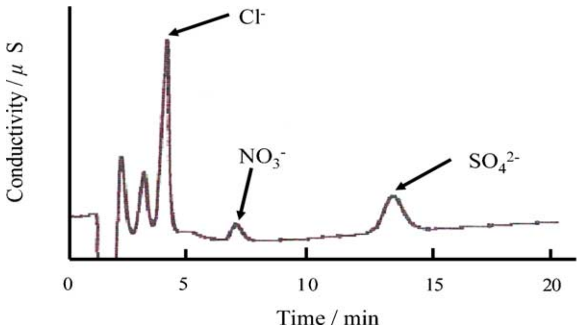

Fig. 4. Chromatogram of the anions in river water, using the anion chromatographic system using on-line recycled eluents, with 1 g of the mixed ion exchange resins in an eluent volume of 100 ml.

recycled eluents with the mixed ion exchange resins column, could not achieve consecutive determination of these anions.

3.3. Consecutive determination of anions in river water

The anion chromatographic system, using on-line recycled eluents with the mixed ion exchange resins in the eluent, was applied to the determination of chloride, nitrate, and sulfate ions in river water. The concentrations of bromide and nitrite ions are generally low in Japanese river waters, so that the anion chromatographic system using on-line recycled eluents could not detect such low levels. The concentrations of chloride, nitrate, and sulfate ions in the river water, using normal IC were 7.3 ± 0.1, 3.4 ± 0.1, and $7.8 \pm 0.1\ \mu\text{g ml}^{-1}$, respectively, where the errors are standard deviations. These values were the same as those using the anion chromatographic system with on-line recycled eluents. The chromatogram of the anions in the river water, using the anion chromatographic system with on-line recycled eluents and mixed ion exchange resins in an eluent volume of 100 ml, is shown in Fig. 4. The chromatogram was completely the same as that using normal IC. The average and RSD values of the retention time and the peak heights, of the three anions on the number of sample injections, are summarized in Table 2. All the RSD values of the peak heights and retention times, in eluent volumes above 100 ml for 50 consecutive determinations of all the anions, were less than 3%. The RSD values, in the anion chromatography using on-line recycled eluents, were the same as those in normal IC. The eluent volume was one tenth less than that used for normal IC, since the nitrite and bromide ions with larger deviations than the other anions were not detected.

4. Conclusions

An anion chromatographic system using on-line recycled eluents to determine chloride, bromide, nitrite, nitrate, and sulfate ions was developed. Although normal IC requires an eluent volume of over 1000 ml to determine these anions, the anion chromatographic system using on-line recycled eluents requires an eluent volume of only 200 ml. Furthermore, the anion chromatographic system using on-line recycled eluents required an eluent volume of only 100 ml to determine chloride, nitrate, and sulfate ions in a river water sample.

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