Ion chromatographic separation of alkali metal and ammonium cations on a C_{18} reversed-phase column

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Abstract

The separation of alkali metal (Li^+, Na^+, K^+, Rb^+ and Cs^+) and ammonium cations on a C_{18} reversed-phase column using three anionic surfactants [sodium 1-eicosyl sulphate, sodium dodecyl benzenesulphonate and sodium dodecyl sulphate (SDS)] is described. Two methods were examined: (a) "permanent" coating, with the use of a C_{18} reversed-phase column previously coated with the surfactants; and (b) dynamic coating, with addition of the surfactants to the mobile phase. With method (a) the separation of the six cations was achieved with SDS. However, the retention times gradually decreased owing to dissolution of the SDS coating. Good separation was obtained with method (b), where 10 mM HNO_3 containing 0.1 mM SDS was used as the mobile phase with conductivity detection, and it was applied satisfactorily to real samples. The effect of system peaks on determination is also discussed.

1. Introduction

Ion chromatography (IC) is a useful technique for the separation and detection of alkali metal and ammonium cations. Low-capacity cation-exchange columns are used for the separation, and various systems of eluents and detection methods have been studied to optimize both separation and detection [1-4]. The elution order is in general $Li^+ < Na^+ < NH_4^+ < K^+ < Rb^+ < Cs^+$ and it almost follows the order of ionic size ($Li^+ < Na^+ < K^+ < NH_4^+$, $Rb^+ < Cs^+$).

On the other hand, reversed-phase columns may be used to separate these cations if cation-exchange groups can be introduced on the surface of the packing material or an electrical double layer can be obtained for cation retention. For anion separation, the use of such columns has been extensively studied and successfully applied to many real samples [5-7]. However, it has hardly been examined for the above cations. If reversed-phase columns can also be used, such columns would have greater flexibility.

The above approach was examined by Molnar et al. [8] and Smith and Pietrzyk [9] for the separation of alkali metal and ammonium cations. However, separation of the six cations was

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not successful. Molnar *et al.*'s method [8] used three long octadecylsilica (ODS) columns (of each 250×4.6 mm I.D.) with 5 mM n-heptane-sulphonate $[CH_3(CH_2)_6SO_3^-]$ solution (pH 2) as a mobile phase. Although the chromatographic peaks of Na$^+$, K$^+$ and NH$_4^+$ appeared at retention times around 9–12 min (flow-rate 2 ml/min), the peaks of Li$^+$ and Na$^+$ and those of NH$_4^+$ and Rb$^+$ overlapped. Smith and Pietrzyk [9] also examined the separation of Na$^+$, K$^+$, NH$_4^+$ and Cs$^+$ using mobile phases containing alkanesulphonate salts $[CH_3(CH_2)_6SO_3^-Li^+$ and $CH_3(CH_2)_7SO_3^-Li^+]$ as additives in H$_2$O–MeOH mixed solvents on a poly(styrene–divinylbenzene) column (150×4.1 mm I.D.). MeOH was added to adjust the exchange capacity in the range 20–40 μM per column. However, even under the best conditions tested the peaks appeared around retention times of 8–11 min and the peak of NH$_4^+$ almost overlapped that of Cs$^+$. The low separability may be mainly due to the small amounts of chemicals sorbed, *viz.*, a lower cation-exchange capacity. Schwedt *et al.* [10] examined the separation of alkali metal cations on an ODS column (250×4 mm I.D.) with a pre-column (50×4 mm I.D.) using various kinds of weak acids and applied the method to wine and mineral water samples. The retention times of Li$^+$, Na$^+$ and K$^+$ were around 7–10 min using 2 mM n-hexylsuccinic acid–1 mM oxalic acid (pH 2.92).

Another method using reversed-phase columns for cation separations is to use neutral ligands such as crown ethers. Crown ether moieties are immobilized on the column surface through covalent bonding, or lipophilic crown ethers are coated by hydrophobic interaction [11,12]. The retention behaviour of crown ether stationary phases depends strongly on the type of crown ether used. For an ODS column coated with dodecyl-18-crown-6, for example, the elution order is Li$^+$ < Na$^+$ < Cs$^+$ < Rb$^+$ < K$^+$. The elution of K$^+$ is retarded, indicating that K$^+$ ion is suitably captured in the cavity of the crown compound. This suggests that good separations may be obtained by using crown compounds designed for the retention of individual analytes. However, such modified ODS columns have the drawback that the retention times change with

the counter anions, because anions with higher polarizability generally enhance the cation complexation of the crown ether.

The purpose of this study was to find the optimum conditions for the mutual separation of alkali metal and NH$_4^+$ cations by using a bonded silica (C_{18}) reversed-phase column. The separation was examined on a column using three anionic surfactants with long alkyl chains [sodium 1-eicosyl sulphate (SES), sodium dodecyl benzenesulphonate (SDBS) and sodium dodecyl sulphate (SDS)]. These surfactants were used for the preparation of previously coated columns and as additives to the mobile phase. Nitric acid was employed as the mobile phase because of its wide use in IC for the separation of alkali metal and ammonium cations [1,3] and the low solubility of the surfactants in acidic solutions. Further, the chromatographic method obtained was compared with conventional IC and was applied to real samples.

2. Experimental

2.1. Chemicals

All inorganic salts were of analytical-reagent grade and used as received. Working standard solutions of alkali metal and ammonium cations were prepared from stock standard solutions (10 g/l) of the chloride and perchlorate salts, prepared using deionized water. SES, SDBS and SDS of analytical-reagent grade, HPLC-grade acetonitrile (AN) and ultra-pure nitric acid were used.

2.2. Ion chromatographic system

The ion chromatograph consisted of a CCPM pump (Tosoh, Tokyo, Japan), a Rheodyne (Cotati, CA, USA) Model 7125 injection valve equipped with a 100-μl sample loop, a CM-8010 conductivity detector (Tosoh) and an SC-8010 chromato-processor (Tosoh). The C_{18} reversed-phase column employed was Capcellpak C_{18} (Shiseido, Tokyo, Japan) of 150 mm $\times$ 4.6 mm I.D., packed with 5-μm spherical particles of octadecyl-bonded silica gel coated with silicone

polymer. The silicone coating permits the use of the column over a wide pH range (2–10), suppressing the undesirable peak tailing of compounds in reversed-phased LC [13,14]. The temperature of the column and the injection valve was maintained at $20 \pm 1°C$.

2.3. Preparation of coated columns and mobile phases

"Permanent" coating system of columns with surfactants

The columns coated with surfactants were obtained by pumping 1 mM aqueous solutions of SDS and SDBS at a flow-rate of 0.5 ml/min until adsorption equilibrium was accomplished. For SES, a 0.2 mM solution in H_2O–AN (75:25, v/v) was employed owing to its low solubility in water. Completion of the column equilibrium was determined by the rapid increase in the conductivity of the effluent from the columns up to a level equal to that of the individual surfactant solution. It was also determined by measuring the total organic carbon (TOC-500 instrument; Shimadzu, Kyoto, Japan) for SDBS and SDS, and by the retention times of cations with SES. The coating solutions were pumped for a further 2–3 h and then switched to 5 mM HNO_3 in order to examine the chromatographic efficiencies. The times taken were *ca.* 17 h for SDS, 23 h for SDBS and 30 h for SES.

Dynamic coating system of columns with SDS

The mobile phases used were 10 mM HNO_3 containing 0.01–0.04 mM SDS, which were prepared from stock standard solutions of 10 mM SDS and 1 M HNO_3. The solutions were filtered through a membrane filter (pore size 0.45 μm) and degassed under reduced pressure prior to use.

2.4. Samples

Tap and pond water were sampled and analysed immediately with the proposed IC system with a C_{18} reversed-phase column, 0.1 mM SDS–10 mM HNO_3 as the mobile phase and conductivity detection. For comparison, the samples were further analysed by a conventional IC

system with conductivity detection (Model IC-100; Yokogawa, Tokyo, Japan) using CX-1 columns $(50 + 250) \times 4.6$ mm I.D. and 5 mM nitric acid as the mobile phase.

3. Results and discussion

3.1. "Permanent" coating system of columns with surfactants

The amounts of surfactant sorbed per column are given in Table 1 for each coating solution, together with that of $CH_3(CH_2)_7SO_3Li$ [9]. The amounts were determined by two methods. One is the determination of Na^+ eluted by 5 mM nitric acid, which was directly switched from the individual coating solution. The amount was determined with a conventional IC system. The other is the difference in the TOC content for the surfactants between the influent and the effluent. The amount of sorbed SES with a long alkyl chain (C_{20}) is very small, in spite of its high hydrophobicity. This is probably due to the addition of acetonitrile to increase the solubility of SES. For SDBS and SDS, the values are relatively large, being comparable to the results from breakthrough volumes.

Fig. 1 shows the separation of alkali metal and ammonium cations on a C_{18} reversed-phase column coated with three anionic surfactants.

Table 1
Amounts of anionic surfactants sorbed

Surfactant	Structure	Amount sorbed[a] (mmol per column)	
		Na⁺	TOC
SES	$CH_3(CH_2)_{19}OSO_3Na$	0.06	–
SDBS	$CH_3(CH_2)_{11}C_6H_4SO_3Na$	0.32	0.36
SDS	$CH_3(CH_2)_{11}OSO_3Na$	0.25	0.24
	$CH_3(CH_2)_7SO_3Li$	0.02[b]	–

[a] C_{18} reversed-phase column (150 × 4.6 mm I.D.) was equilibrated with 0.1 mM SES in AN–H_2O (25:75, v/v) and 1 mM DBS and SDS in H_2O, respectively.
[b] Ref. 9. Poly(styrene–divinylbenzene) copolymeric reversed-phase column (150 × 4.1 mm I.D.) was equilibrated with a 2.5 mM solution in MeOH–H_2O (20:80, v/v).
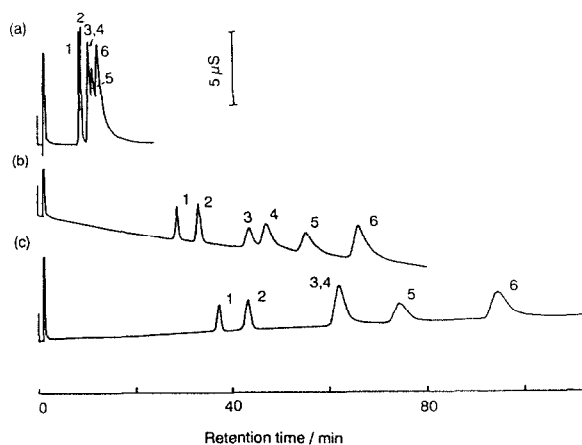
Fig. 1. Ion chromatograms of alkali metal and ammonium cations. C_{18} reversed-phase column coated with anionic surfactants: (a) 0.2 mM SES in H_2O–AN (75:25, v/v); (b) 1 mM SDS; (c) 1 mM SDBS. Mobile phase, 5 mM HNO_3; conductivity detection; flow-rate, 1.0 ml/min; sample, chloride salts, 100 μl. Peaks; 1 = Li^+ (0.45 mg/l); 2 = Na^+ (2 mg/l); 3 = NH_4^+ (2 mg/l); 4 = K^+ (7.5 mg/l); 5 = Rb^+ (20 mg/l); 6 = Cs^+ (50 mg/l).

The mobile phase used was 5 mM nitric acid and the flow rate was 1 ml/min. Fig. 1a shows the chromatogram obtained with the column coated with SES: the order of retention times ($Li^+ <$ $Na^+ < NH_4^+$, $K^+ < Rb^+ < Cs^+$) was the same as the order obtained by conventional IC with nitric acid [1,3]. No dissolution of the SES coating was observed. However, the volumes were small and the separability was poor, mainly owing to low ion-exchange capacity. For SDBS (Fig. 1c), the separation of K^+ and NH_4^+ could not be achieved in spite of the large retention time. The retention volumes of the six cations were almost constant up to pumping ca. 2.2 l of 5 mM HNO_3 (37 h), although the SDBS coating level decreased from 0.32 to 0.18 mmol per column. This suggests that the effective ion-exchange capacity was almost constant until that concentration of SDBS. When SDS was used, the six cations were separated as shown in Fig. 1b. However, the retention times decreased rapidly owing to the dissolution of SDS with weak hydrophobicity. For example, pumping 400 ml of 5 mM HNO_3 resulted in a ca. 50% decrease in the amount of SDS sorbed. This suggests that SDS should be

present in the mobile phases to obtain constant retention times.

3.2. Dynamic coating system of column with SDS

Fig. 2 shows typical ion chromatograms of the six cations using three mobile phases containing SDS at different concentrations (Fig. 2a, 0.1 mM; b, 0.2 mM; c, 0.4 mM). A 10 mM HNO_3 concentration was adopted for the mobile phase for faster elution of the cations. There were no differences in the retention times of the cations between chloride and perchlorate salts, unlike the results with crown compounds [11,12]. Smith and Pietrzyk [9] suggested that the retention of analyte cations was directly proportional to the hydrophobic ion concentration. However, under the conditions they used [$CH_3(CH_2)_6SO_3^- Li^+$ and $CH_3(CH_2)_7SO_3^- Li^+$ in H_2O–MeOH mixtures], the amount of hydrophobic ions sorbed on the poly(styrene–divinylbenzene) resin was not sufficient to separate four cations (Na^+, K^+, NH_4^+ and Cs^+). The retention times increased with concentration of SDS in the mobile phases and were stable, suggesting that the retention times in this system were controllable. The 0.1
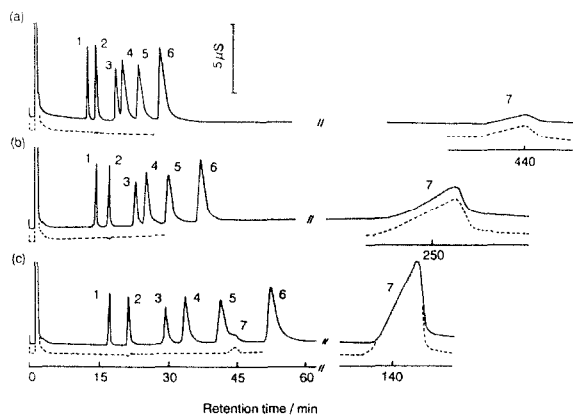

Fig. 2. Ion chromatograms of alkali metal and ammonium cations using a C_{18} reversed-phase column. Mobile phase: (a) 0.1 mM SDS; (b) 0.2 mM SDS; (c) 0.4 mM SDS; each mobile phase contained 10 mM HNO_3. Conductivity detection; flow-rate, 1.0 ml/min; sample, 100 μl. Solid lines, as in Fig. 1; dashed lines, pure water. Peaks: 1 = Li^+; 2 = Na^+; 3 = NH_4^+; 4 = K^+; 5 = Rb^+; 6 = Cs^+; 7 = system peak.

mM SDS–10 mM HNO$_3$ system was effective with respect to separation efficiency and the shorter retention times.

The appearance of system peaks, as shown in Fig. 2, was as follows. (1) The system peak increased in intensity with increase in SDS concentration but with decreased retention times. For 0.4 mM SDS, a small system peak was observed around 45 min (Fig. 2c). (2) The peak intensity of a standard solution was smaller than that of pure water but they gave the same retention times. (3) The system peaks were not observed when using both a standard solution and pure water containing SDS and HNO$_3$ at the same concentration as that in the mobile phase.

From the above results, the following conclusions can be drawn. In acidic condition (10 mM HNO$_3$), added SDS exists mainly as dodecylsulphuric acid (DSA) in both the mobile and solid phases. The injection of standard solutions or H$_2$O causes the elution of sorbed DSA. Hence the system peak may be attributed to the desorption and adsorption of DSA (neutral eluent molecules) from the column surface, taking account of the results for anions [15]. Accordingly, the disturbance from the desorption–adsorption equilibrium increases with increasing concentration of SDS, but on the other hand the retention times decreases. The retention of DSA in a standard solution will be larger than that of pure water, owing to the salting-out effect [16]. The small system peak for a 0.4 mM concentration may be attributed to SDS. From the viewpoint of determination, a 0.1 mM SDS system is better because of the low intensity of the system peak and the long retention time, as shown in Fig. 2a.

The detection limits with the 0.1 mM SDS–10 mM HNO$_3$ system were 0.004 (Li$^+$), 0.1 (Na$^+$), 0.02 (NH$_4^+$), 0.08 (K$^+$), 0.2 (Rb$^+$) and 0.4 mg/l (Cs$^+$) for a signal-to-noise ratio of 2. These values are larger than those with indirect UV and fluorimetric detection [0.01 mM Ce(III) mobile phase and a IC column] [2] and with conductivity detection (2 mM HNO$_3$ mobile phase) [3]. This is mainly due to both the larger retention times and background conductivity with 10 mM HNO$_3$. The lower detection limit of Na$^+$ is due
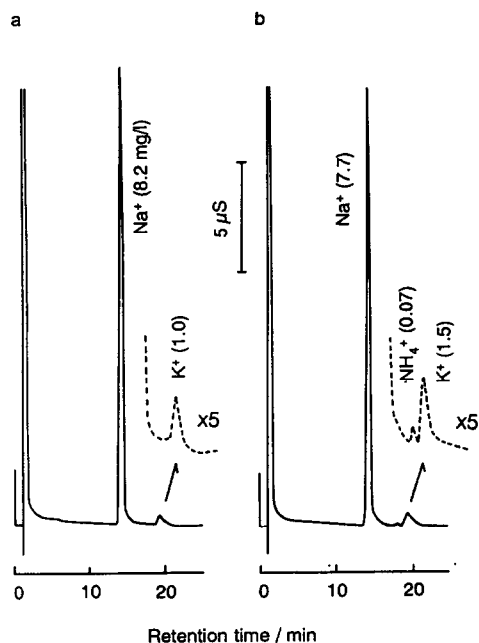

Fig. 3. Ion chromatograms of (a) tap water and (b) pond water. Mobile phase, 0.1 mM SDS–10 mM HNO$_3$. Other conditions as in Fig. 2.

to the addition of SDS and is improved (0.02 mg/l) by using lithium dodecyl sulphate as an additive.

3.3. Analysis of samples

Fig. 3 shows ion chromatograms of tap and pond water and Table 2 gives the results obtained by both the present and conventional IC methods. The results obtained by the peak-height method correspond well with those ob-

Table 2
Analytical results (mg/l) obtained by the present method and a conventional IC method

Sample	Method	Na$^+$	NH$_4^+$	K$^+$
Tap water	Present	8.2	N.D.	1.0
	IC	7.8	N.D.	1.1
Pond water	Present	7.7	0.07	1.5
	IC	7.5	0.08	1.8

tained by a conventional IC system, suggesting that the present SDS addition system is useful for the determination of alkali metal and ammonium cations.

In conclusion, the separation of alkali metal and ammonium cations could be achieved by the addition of SDS to the mobile phase. Although the system obtained has larger retention times compared with conventional IC, the use of a C_{18} reversed-phase column, which has several advantages compared with "fixed-site" ion-exchange columns, may have various applications because of the wide flexibility in the choice of mobile phases.

4. References

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