Short communication

Separation behavior of inorganic anions on an octadecyl-bonded silica column coated with cetyltrimethylammonium by phthalate and salicylate eluents

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Abstract

The separation behavior of seven common inorganic anions on an octadecyl-bonded silica (ODS) column coated with cetyltrimethylammonium (CTA^+) by phthalate and salicylate eluents was examined with indirect UV detection. The separation became better with increasing anion-exchange capacity for the phthalate eluent, but not for the salicylate eluent. The CTA^+-coated column, equilibrated with 1 mM CTA^+ in water–methanol (MeOH) (80:20, v/v) (anion-exchange capacity, 0.26 mequiv./column) and 1.5 mM sodium phthalate eluent (pH 6.8) was effective for the determination of inorganic anions in river and pond water samples.

Keywords: Cetyltrimethylammonium coating; Stationary phase, LC; Water analysis; Coating; Inorganic anion; Phthalate

1. Introduction

Ion chromatography (IC) of anions usually employs low-capacity anion-exchange columns. However, it is possible to use reversed-phase columns such as octadecyl-bonded silica (ODS) and polymer-based resin columns [1–5]. Two methods are usually employed for anion separation on reversed-phase columns: (A) dynamic coating and (B) permanent coating. Although method (A) only has additives in the eluents, which makes it simple to operate, a particular drawback is the appearance of system peaks due to eluent anions. On the other hand, as method (B) does not have any coating reagents in the eluents, the reversed-phase columns can be used as separation columns with fixed anion-exchange sites. In addition, both the anion-exchange capacity

of the columns and the concentration of eluents can be changed independently, thus flexibility is higher for anion separation of various samples.

As an example, ppb levels of NO_2^- and NO_3^- in sea water and inorganic salts of reagent grade were directly determined without interference of excess of anions such as Cl^- and Br^-, using a CTA^+-coated ODS column with higher exchange capacity, 0.1 M NaCl eluent, and direct UV and electrochemical (glassy carbon electrode) detection [6,7]. However, the determination of NO_2^- and NO_3^- by conventional IC columns with lower anion-exchange capacity was impossible because of interference by the coexisting anions. The ODS columns coated with quarternary ammonium were also examined as an alternative to the conventional IC columns [8–11]. However, the merit of coated columns has not been well examined.

In this study, the separation behavior of seven common inorganic anions, F^-, Cl^-, NO_2^-, Br^-, NO_3^-, $H_2PO_4^-$, SO_4^{2-} was examined by CTA^+-coated ODS columns with various exchange capacities, phthalate and salicylate eluents, and indirect UV detection. The permanent coating system was compared to the dynamic coating system and applied to real water samples.

2. Experimental

2.1. Apparatus

The ion chromatographic system consisted of (a) a pump (CCPM; Tosoh, Tokyo, Japan); (b) an injector with 100 µl sample loop (Rheodyne 7125; Cotati, CA, USA); (c) a UV detector (L-4200; Hitachi, Tokyo, Japan); (d) a chromato-processor (SC-8010; Tosoh).

2.2. Column and mobile phase preparation

The ODS column employed was a Capcellpak C_{18} AG-120Å (Shiseido, Tokyo, Japan; 150 mm×4.6 mm I.D., particle size 5 µm, octadecyl-bonded silica gel coated with silicone polymer).

For permanent coating, the ODS column was equilibrated with 1 mM cetyltrimethylammonium chloride (CTAC) in water–MeOH mixtures (MeOH volume fraction, 0–44%) at 20°C. After washing with deionized water (ca. 5 ml), the column was converted to phthalate or salicylate anion forms by sodium phthalate/salicylate eluents. The anion-exchange capacities of the CTA^+-coated columns were determined from breakthrough volumes of phthalate or salicylate eluents.

3. Results and discussion

3.1. Separation by permanently CTA^+-coated column

In a permanent coating system, the column can be considered as an anion-exchange column with fixed

exchange sites. If the equilibrium shown in Eq. (1) is valid,

$$yE^{x-} \cdot R_x + xS^{y-} \rightleftharpoons yE^{x-} + xS^{y-} R_y \qquad (1)$$
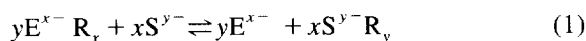
(E^{x-}, the eluent anion; S^{y-}, the sample anion; R_y, R_x, the exchange sites on the stationary phase; $K_{E,S}$, the selectivity coefficient), Eq. (2) can be derived [1],

$$\log k' = 1/x \log K_{E,S} + y/x \log([capacity]/x)$$
$$+ \log w/V_m - y/x \log[E^{x-}] \qquad (2)$$

where k' is capacity factor, w is the mass of the stationary phase, and V_m is the volume of mobile phase.

Eq. (2) indicates that when the ratios of anion-exchange capacity of the CTA^+-coated column and eluent concentration, [capacity]/[E^{x-}], are the same, anion separations are almost identical in spite of differences in anion-exchange capacities. The slope between $\log k'$ and $\log[E^{x-}]$ is $-y/x$. However, the permanent coating may change surface properties of the stationary phase and thus may result in different anion separations for various mobile phase systems.

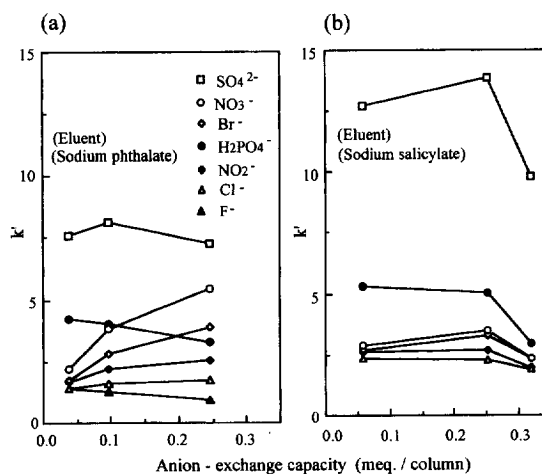Fig. 1 shows the correlation between the capacity

Fig. 1. Dependence of anion separation on anion-exchange capacity of column. Column= ODS column permanently coated with cetyltrimethylammonium. Mobile phase = (a) sodium phthalate (0.4, 0.8, 1.5 mM, pH 6.8) and (b) sodium salicylate (0.5, 1.5, 2.5 mM, pH 5.8, 6.4, 6.4, respectively) containing 5% (v/v) acetonitrile. The order of mobile phases used was based on increase in anion-exchange capacities.

factors (k') of anions and anion-exchange capacities of CTA^+-coated column. The concentrations of eluents in this figure were selected for retention times of SO_4^{2-} to be in the range of 10–11 min and 15–20 min for phthalate and salicylate eluents, respectively.

For phthalate eluent (Fig. 1a), although the k' values of PO_4^{3-} and SO_4^{2-} were almost the same, the separation of other anions became better with increase in anion-exchange capacity. Good chromatogram of seven inorganic anions was obtained for the column with anion-exchange capacity of 0.26 mequiv./column (Fig. 2). For the plot of log k' – log [E^{x-}] for the column with anion-exchange capacity of 0.26 mequiv./column, the slope ($-y/x$ in Eq. (2)) was -0.53 ± 0.02 for F^-, Cl^-, NO_2^-, Br^-, and NO_3^- and -1.05 and -0.66 for SO_4^{2-} and $H_2PO_4^-$, respectively, which agreed well with the calculated slopes of -0.52, -1.05 and -0.60, respectively. The concentration of eluent (E^{x-}) examined was 0.8, 1.5 and 3.0 mM sodium phthalate (pH 6.4). The effective charge at pH 6.4 is -1.91 for phthalate eluents ($pK_{a1,2}$, 2.95, 5.41) and -1.14 for phosphate ion ($pK_{a1,2,3}$, 2.15, 7.20, 12.38). These results suggest that the CTA^+-coated column with higher exchange capacity can be used as a conven-
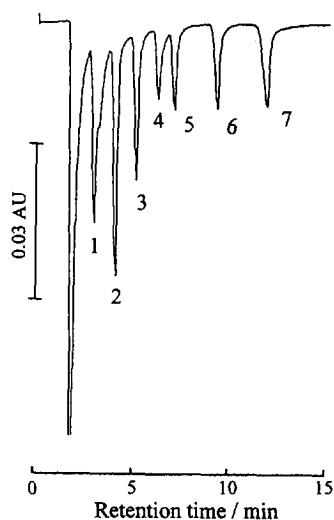
tional IC column. On the other hand, the separation by salicylate eluents was not good for Cl^-, NO_2^-, Br^-, and NO_3^- and the elution of SO_4^{2-} was delayed. This pattern was not improved in spite of the increase in exchange capacity (Fig. 1b). A 3 mM p-hydroxybenzoate eluent (crystal violet-coated ODS column) was effective in alkaline solution (pH 8) [8]. However, the alkaline solution decreased the separation efficiency of C_{18} column. For CTA^+-coated ODS column–0.5 mM trimellitate eluent (pH 6) system, the elution of $H_2PO_4^-$ was near F^-, and that of SO_4^{2-} was after NO_3^- [11].

The separation of anions by the CTA^+-coated column system was compared to that by the dynamic coating system using the tetrabutylammonium cation (Bu_4N^+) for phthalate (($Bu_4N)_2$Pht, 0.2–0.6 mM, pH 5.9–6.1) and salicylate [($x-0.1$ mM) $Bu_4NOH/$ x mM salicylic acid (x=0.4–1.0, pH 3.6–3.8)] systems. The separation of anions was good for the phthalate system. However, the elution of SO_4^{2-} was delayed and a large system peak due to the eluent appeared after SO_4^{2-} for both indirect UV and conductivity detection. The delay in SO_4^{2-} retention was a little improved by using higher phthalate concentrations and the addition of Bu_4NI (2–8 mM) to the phthalate eluent.

3.2. Application to real water samples

For the phthalate system using a CTA^+-coated column with anion-exchange capacity of 0.26 mequiv./column, the retention of $H_2PO_4^-$ increased with the increase in pH of the 1.5 mM phthalate eluent. A pH of 6.8 was selected for good separation between $H_2PO_4^-$ and NO_3^- or Br^-. As the solubility of CTA^+ is small in this eluent, the decrease in anion retention was very small. For example, the retention volume of SO_4^{2-} for 1.5 mM sodium phthalate (pH 6.8) decreased slightly from 12.2 to 11.6 min for successive flow of 100 h at a flow-rate of 1.0 ml/min. Further, the addition of 0.01 mM CTAC (flow-rate 1 ml/min for 6 h) to the eluent recovered retention time of 0.2 min for SO_4^{2-}, keeping good separation for the seven anions. Fig. 3 shows the ion chromatograms of river and pond waters, filtered through a 0.45 μm membrane filter. A peak preceding Cl^- was that of HCO_3^-, which was confirmed by its disappearance after the addition of dilute nitric

Fig. 2. Ion chromatogram of inorganic anions, (1) F^-, (2) Cl^-, (3) NO_2^-, (4) $H_2PO_4^-$, (5) Br^-, (6) NO_3^-, (7) SO_4^{2-} (10 mg/l each). Anion-exchange capacity of CTA^+-coated column, 0.26 mequiv./column; mobile phase, 1.5 mM sodium phthalate (pH 6.8); UV detection, 277 nm; flow-rate, 1.0 ml/min.; sample volume, 100 μl.
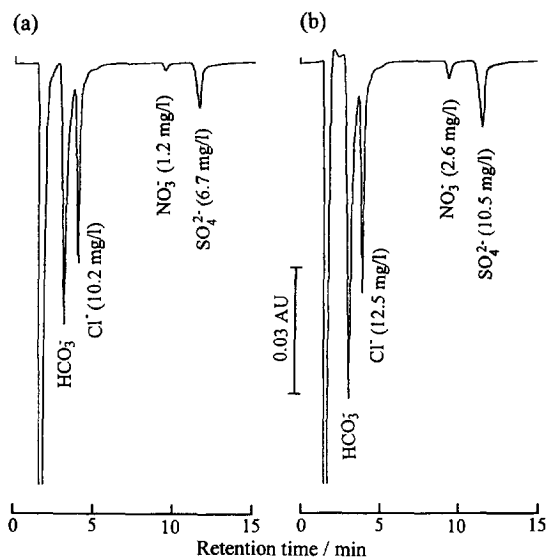
Fig. 3. Ion chromatograms of inorganic anions in (a) river and (b) pond waters. Conditions were the same as in Fig. 2.

acid in the samples. Detection limits by indirect UV detection were 0.02 mg/l (Cl$^-$), 0.02 (NO$_3^-$), and 0.05 (SO$_4^{2-}$).

References

[1] P.R. Haddad and P.E. Jackson, Ion Chromatography: Principle and Applications, Elsevier, Amsterdam, 1990.

[2] P.K. Dasgupta, in J.G. Tarter (Editor), Ion Chromatography, Marcel Dekker, New York, 1987, pp. 253–272 and references cited therein.

[3] R.M. Cassidy and S. Elchuk, Anal. Chem, 54 (1982) 1558.

[4] R.M. Cassidy and S. Elchuk, J. Chromatogr. Sci., 21 (1983) 454.

[5] D.L. Duval and J.S. Fritz, J. Chromatogr., 295 (1984) 89.

[6] K. Ito, Y. Ariyoshi, F. Tanabiki and H. Sunahara, Anal. Chem., 63 (1991) 273.

[7] K. Ito, Y. Ariyoshi and H. Sunahara, J. Chromatogr., 598 (1992) 237.

[8] G. Müller and H.-U. Meisch, J. Chromatogr., 483 (1989) 145.

[9] K. Ito, E. Shoto and H. Sunahara, J. Chromatogr., 549 (1991) 265.

[10] Y. Michigami, K. Fujii and K. Ueda, J. Chromatogr. A, 664 (1994) 117.

[11] K. Ohta and K. Tanaka, Bunseki Kagaku, 44 (1995) 713.