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Note

Indirect photometric detection of inorganic anions in micro high-performance liquid chromatography with permanently coated columns

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Ion chromatography has been widely applied to the analysis of inorganic ions as well as organic ions since it was initiated by Small *et al.*[1]. Indirect photometric detection is one of the detection methods employed in ion chromatography, in which the analyte ions displace the UV-absorbing mobile phase ions, resulting in a depression of the background signal[2].

Ion-exchange columns obtained by permanent coating of an ODS column[3], a silica gel column[4] and a polystyrene resin[5] with hydrophobic ions have been investigated for ion chromatography. The ion-exchange capacities of these columns can easily be controlled by changing the coating conditions such as the concentration of the coating solution and the composition of the matrix solution. Microcolumns facilitate examination of the preparation conditions for these permanent coatings.

The use of microcolumns in ion chromatography has been investigated by Rokushika *et al.*[6–8]. They used microcolumns packed with commercially available ion exchangers or polyallylamine-coated silica gel.

This paper describes ion chromatography using micro anion-exchange columns prepared by permanent coating of an ODS column with the hydrophobic cetyltrimethylammonium ion. The analyte anions are detected indirectly by using an UV detector.

EXPERIMENTAL

Apparatus

The liquid chromatograph comprised a Microfeeder (Azumadenki Kogyo, Tokyo, Japan) equipped with an MS-GAN 050 gas-tight syringe (0.5 ml; Ito, Fuji, Japan), an ML-422 micro valve injector (0.02 μl; Jasco, Tokyo, Japan), a micro fused-silica column, a laboratory-made water-bath and an UVIDEC-100V UV spectrophotometer (Jasco) with a modified flow cell. The separation column was immersed in the water-bath in order to decrease the effect of variations in the room temperature. The temperature of the water was not regulated.

Column preparation

Develosil ODS-3K (particle diameter 3 μm; Nomura Chemical, Seto, Japan)

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was employed as the octadecylsilica packing material. This material was packed into fused-silica tubing (100 mm × 0.32 mm I.D.) by a slurry packing method. An appropriate volume of cetyltrimethylammonium bromide (cetrimide) solution was passed into the prepared ODS column, followed by washing with deionized water. The breakthrough volume of the anion-exchange column was measured by using an aqueous solution of 1 m*M* sodium salicylate.

Reagents

All the reagents employed were of reagent grade and were obtained from Wako (Osaka, Japan), unless otherwise noted. Deionized water was prepared by use of a MILLI-Q4 water purification system (Millipore, Bedford, MA, U.S.A.). The sample solution and the mobile phase were prepared with deionized water.

RESULTS AND DISCUSSION

The amounts of cetrimide introduced into the ODS column can be controlled by the concentration of cetimide in the coating solution and the composition of the coating matrix solution (a mixture of an organic solvent and water). The amounts increases with increasing concentration of cetrimide and/or the water content in the coating solution, and they can be estimated from the breakthrough volume of sodium salicylate and its concentration. When 0.25 ml of 1, 3 or 5 m*M* cetrimide dissolved in methanol–water (50:50) were passed into ODS columns of 100 mm × 0.32 mm I.D., the amounts of salicylate ions introduced onto the permanently coated columns were $1.3 \cdot 10^{-7}$, $8.9 \cdot 10^{-7}$ and $1.2 \cdot 10^{-6}$ mol, respectively. If we assume that no hydrophobic adsorption of salicylate occurs on the prepared columns, these values can be regarded as the ion-exchange capacities of the columns. Actually, the amount of sodium salicylate adsorbed on the ODS column due to the hydrophobic interaction was $1.2 \cdot 10^{-8}$ mol when a 1 m*M* aqueous solution of sodium salicylate was passed through it. This value was much smaller than that, for the permanently coated col-

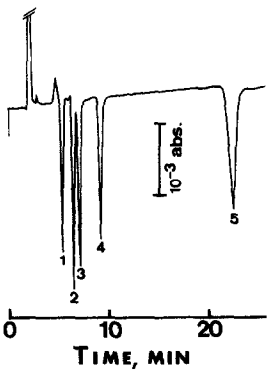

Fig. 1. Separation of inorganic anions on a permanently coated column. Column: 100 mm × 0.32 mm I.D., permanently coated with 3 m*M* cetrimide dissolved in methanol–water (50:50). Mobile phase: 1 m*M* sodium salicylate containing 5% acetonitrile. Flow-rate: 2 μl/min. Samples: 1 = chloride; 2 = bromide; 3 = nitrate; 4 = chlorate; 5 = sulphate; 0.02 μl containing 1 m*M* of each was injected. Wavelength of UV detection: 230 nm.

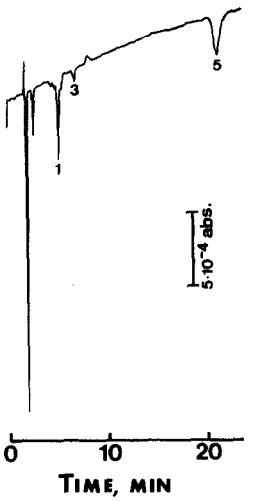

Fig. 2. Separation of anions in tap-water. Operating conditions as in Fig. 1 except for the sample: 0.02 μl of tap-water, peak numbers as in Fig. 1.

umns. However, it is reasonable to use an hydrophilic anion such as nitrate as the reagent for measurement of the ion-exchange capacity.

The retention times of anions increased with increasing amounts of salicylate introduced, as expected. The chromatographic retention behaviours of the columns prepared were the same as those commonly observed in ion chromatography[9].

Fig. 1 demonstrates the separation of an artificial mixture of inorganic anions using a 1 m*M* sodium salicylate aqueous solution containing 5% acetonitrile (pH 5.8) as the mobile phase. This column was prepared by using a solution of 3 m*M* cetrimide dissolved in methanol–water (50:50). The analyte anions appeared as negative peaks, while a non-retained system peak was observed as a positive peak. The retention times of the anions were longer than those observed when an aqueous solution of sodium salicylate was used as the mobile phase. This result may be due to the decrease in the degree of dissociation of sodium salicylate caused by the addition of acetonitrile.

The concentration of each analyte in Fig. 1 is 1 m*M*, which corresponds to 0.7–1.9 ng injected. The concentration detection limits at a signal-to-ratio, S/N = 2 were *ca.* 0.02 m*M* (0.7–1.9 ppm), corresponding to mass detection limits of 14–38 pg. Such low mass detection limits are due to the use of microcolumns. The concentration detection limits were improved by a factor of ten by using a valve injector with an injection volume of 0.2 μl (Model 7520; Rheodyne, Cotati, CA, U.S.A.). However, the concentration detection limits were poorer than those achieved by conventional columns with electrical conductivity detection[10]. Precolumn enrichment will improve the concentration detection limits in microcolumn ion chromatography.

A good linear relationship between the peak height and the concentration of the analyte anions up to 1 m*M* (62 ppm) was observed.

Fig. 2 demonstrates the separation of the anions contained in tap-water in which chloride (10 ppm), nitrate (2.2 ppm) and sulphate (21 ppm) are detected.

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