CHROM. 23 305

Ion chromatography of inorganic iodine species using C_{18} reversed-phase columns coated with cetyltrimethylammonium

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(First received November 13th, 1990; revised manuscript received March 5th, 1991)

ABSTRACT

Low-capacity anion-exchange columns were developed by sorption of cetyltrimethylammonium on two types of C_{18} reversed-phase columns which were coated with 1 mM cetyltrimethylammonium in water–methanol mixtures (57:43, v/v, to 45:55, v/v) at 20°C. The exchange capacities of the columns were estimated by three methods. The high separation efficiency for anions was performed by using a 0.1 M sodium chloride–5 mM sodium phosphate buffer (pH 5.8) as mobile phase. An ion chromatographic system for iodide consisted of the column (polymer-coated silica packing) coated with 1 mM cetyltrimethylammonium in water–methanol (56:44%, v/v), the sodium chloride mobile phase, and ultraviolet or amperometric detection. Good chromatograms for iodide in surface sea waters were obtained without interference by an excess of salts.

INTRODUCTION

Anion separation has been carried out by using low-capacity anion-exchange columns [1–4] and reversed-phase columns [5–15]. For the latter, some alkylammoniums have been added to mobile phases [6,13–15] or coating solutions [8–12]. For the preparation of coated columns, long-chain quaternary ammoniums such as cetyltrimethylammonium (CTA^+) have been employed [8–12]. The coated columns have a wide applicability for anion determination, because anion-exchange capacities can be controlled by using various coating conditions for practical purposes. However, this technique and its advantage have rarely been applied to real samples.

Direct determination of trace-level nitrite and nitrate in sea water by use of coated column has previously been reported by the authors [11]. The ion chromatographic system employed consisted of C_{18}-silica (silicone-coated packing material) columns coated with CTA^+ which had higher exchange capacity, 0.1 M sodium chloride–5 mM sodium phosphate (sodium hydrogenphosphate–sodium dihydrogenphosphate) buffer (pH 5.8) as mobile phase, and UV or amperometric (AMP) detection. The interference of an excess of Cl^- in sea water could be removed by use of a high concentration of sodium chloride in the mobile phase because there was no retention of Cl^- on the column in the Cl^- form. Further, the mobile phase stabilized

the retention of CTA^+ on the column and did not disturb UV and AMP detection. This system (mobile phase, detection method) was also applied to direct determination of iodide in sea water using a low-capacity anion-exchange column [3,4]. However, the coated columns with high capacity could not be applied to sensitive detection of iodide because of a larger retention volume.

The separation of iodide on C_{18} reversed-phase columns has been achieved using the mobile phases acetonitrile–2 mM tetrabutylammonium hydroxide–40 mM phosphate buffer (pH 6.0) (5.0:47.5:47.5) [13] and 0.01 M octylamine adjusted to pH 6.2 with orthophosphoric acid [14]. The column coated with tridodecylmethylammonium and the mobile phase 0.2 M sodium dihydrogenphosphate–0.039 M sodium phosphate (pH 6.4) was also effective [12].

In this study, the column efficiency of the coated columns with low capacity, which were coated with methanol-rich solutions of 1 mM CTA^+, by the use of 0.1 M sodium chloride mobile phase was investigated in order to extend the usefulness of the coated columns. The results were compared with the previous results obtained by using a conventional ion chromatography column [3,4]. Further, the system was applied to detection of iodine species (I^- and I^- + IO_3^-; IO_3^- was reduced to I^- [16,17]) in sea water.

EXPERIMENTAL

Apparatus

The ion chromatographic system employed in this study was identical to that described previously [11]: (a) a Tosoh Model CCPM pump; (b) a Rheodyne 7125 injector (100-μl sample loop); (c) a Hitachi Model L-4200 UV detector; Yanagimoto Models VMD-101A and P-1000 amperometric (AMP) detectors using a glassy carbon working electrode; (d) a Tosoh CP-8000 chromatoprocessor.

Column

Two types of C_{18} reversed-phase columns were Capcellpak C_{18} (Shiseido, 150×4.6 mm I.D., particle size 5 μm, octadecyl-bonded silica gel coated with silicone polymer [18,19] and TSKgel ODS-80T$_M$ (Tosoh, 150×4.6 mm I.D., particle size 5 μm, octadecyl-bonded silica gel). The columns were equilibrated with 1 mM cetyltrimethylammonium chloride (CTAC, used as received) in various water–methanol mixtures [methanol concentration 43–55% (v/v), HPLC grade] at $20 \pm 0.05°$C. The solutions were pumped through the columns at a flow-rate of 0.5 ml/min. The methods for (a) determination of completion of the column coating and (b) determination of amount of sorbed CTA^+ were identical to those described previously [11]. After washing with water, the columns were used for the separation of inorganic anions. The mobile phase used was 0.1 M sodium chloride–5 mM sodium phosphate buffer (pH 5.8) and the flow-rate was maintained at 1.0 ml/min. Separations and measurements were carried out at room temperature (*ca.* 25°C).

Reagent

All inorganic salts were of analytical reagent grade. Inorganic sodium salts were used for the preparation of stock solutions of each anion (10–50 g/l) and the mobile phase (0.1 M sodium chloride). Artificial sea waters (salinity 0–45‰) were prepared

according to the Lyman–Fleming formula [20]. All solutions were prepared in distilled, deionized water and filtered through a 0.45-μm membrane filter before use.

Analysis of iodine species in sea water

For iodide, surface sea waters of the Seto Inland Sea, which were sampled near Hiroshima City, were filtered through a 0.45-μm membrane filter within 24 h of collection, pretreated by passage through a Sep-Pak C_{18} cartridge (Waters Assoc.), and directly injected [UV (226 nm) and AMP ($+1.0$ V *vs.* Ag/AgCl) detection]. For total inorganic iodine ($I^- + IO_3^-$), 0.02 M ascorbic acid (0.25 ml) and 3 M acetic acid (0.25 ml) were added to the samples (24.5 ml) for reduction of iodate to iodide. The samples, which were shaken for 2 min, were injected (UV detection). The iodide and total iodine were determined from the peak area with reference to calibration standards (35‰ artificial sea water) and its solutions containing the reductants, respectively.

RESULTS AND DISCUSSION

Preparation of columns with low capacity

The amounts of sorbed CTA^+ on two C_{18} reversed-phase columns, Capcellpak C_{18} and TSKgel ODS-80T$_M$, could be easily controlled by the addition of methanol in 1 mM CTAC coating solutions. Fig. 1 shows the variation of the amount of sorbed CTA^+ with methanol concentration (40–55%, v/v) in coating solutions. The amount of sorbed CTA^+ decreased rapidly with increasing amount of methanol. The anion-exchange capacities of the coated columns with 43 and 45% (v/v) methanol were estimated by three methods: (1) the amount of sorbed CTA^+; (2) the determination of nitrate onto anion-exchange sites; (3) the breakthrough volume of salicylate [11]. The results are summarized in Table I. They indicate that the sorbed CTA^+ almost works
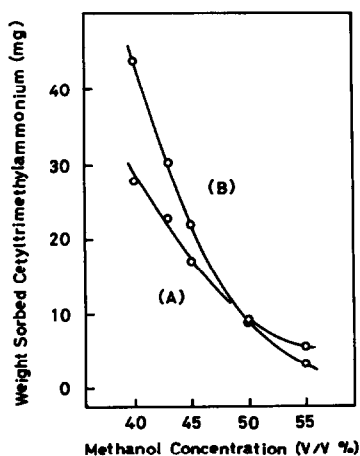

Fig. 1. Variation of amount of sorbed cetyltrimethylammonium with concentration of methanol in coating solution. C_{18} reversed-phase column: (A) Capcellpak C_{18} and (B) TSKgel ODS-80T$_M$. Coating conditions are given in the Experimental section.

TABLE I

ANION-EXCHANGE CAPACITIES OF COLUMNS COATED WITH CTA$^+$

Solution water–methanol (%, v/v)	Column	Exchange capacity (mequiv. per column)		
		CTA$^+$ sorbed	Salicylate	Nitrate
57:43	Capcellpak C$_{18}$^{a}	0.073	0.068	0.059
	TSKgel ODS-80T$_M$^{a}	0.098	0.083	0.088
55:45	Capcellpak C$_{18}$	0.059	0.050	0.046
	TSKgel ODS-80T$_M$	0.077	0.068	0.065
–	TSKgel IC-Anion-PW^b	–	–	0.066

^{a} The columns were coated with 1 mM CTAC in water–methanol mixtures at 20°C.
^{b} The supplier's value was 0.07 mequiv. per column.

as an anion-exchange site and the anion-exchange capacities are similar to a conventional IC column, TSKgel IC-Anion-PW.

Separation of iodide

Fig. 2 shows the corrected retention volumes of seven inorganic anions on two columns coated with methanol-rich solutions. The anions (1 mg/l each) were separated by using a mobile phase of 0.1 M sodium chloride–5 mM sodium phosphate buffer (pH 5.8). The same results as regards retention volumes were also obtained using other columns. Sodium chloride in the mobile phase at a concentration of 0.1 M
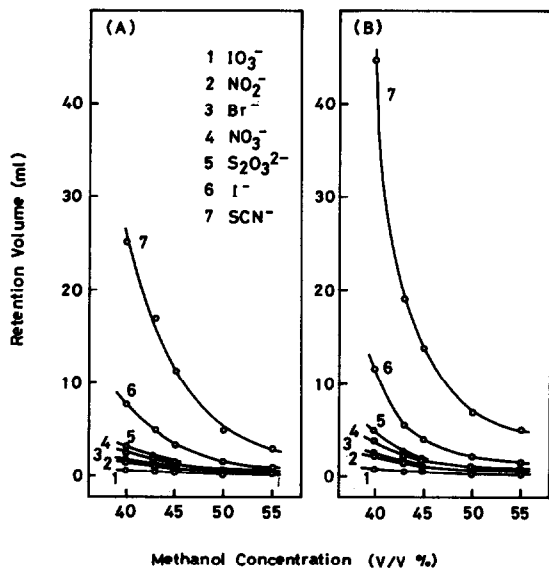

Fig. 2. Variation of retention volume of inorganic anions with concentration of methanol in coating solution. Conditions: column, (A) Capcellpak C$_{18}$ and (B) TSKgel ODS-80T$_M$; mobile phase, 0.1 M sodium chloride–5 mM sodium phosphate buffer (pH 5.8).

stabilized the sorbed CTA$^+$, probably because of the reduction of ionic repulsion among CTA$^+$s and enhancement of hydrophobic interactions of CTA$^+$s with octadecyl groups [11]. In this study, the retention volumes of anions on columns coated with 44% methanol were constant for a successive flow (30 h; flow-rate of 1.0 ml/min), and the coated column (Capcellpak C$_{18}$) could be used for a series of studies without coating (2 weeks).

For both columns the retention volume of each anion decreased with increasing methanol concentration, $i.e.$ decreasing the amount of sorbed CTA$^+$. The retention volumes of anions on Capcellpak C$_{18}$ were small compared with those on TSKgel ODS-80T$_M$ over the methanol concentration studied. However, the amount of sorbed CTA$^+$ (Capcellpak C$_{18}$) was similar to TSKgel ODS-80T$_M$ for 50% methanol and larger for 55% methanol (Fig. 1). For 40–45% (v/v) methanol, iodide was well separated from hydrophilic anions (iodate, nitrite, bromide, nitrate and thiosulfate) and thiocyanate with lower hydration energy. Thus, it was found that the separation system (the coated column and mobile phase) for iodide is reasonable.

Fig. 3A and B show separation of inorganic anions on Capcellpak C$_{18}$ coated with a water–methanol (56:44, v/v) solution. Good chromatograms and flat baselines were obtained by both UV (226 nm) and AMP ($+$ 1.0 V $vs.$ Ag/AgCl) detection. The column which is coated with silicone polymer gains resistance to the alkaline solution (up to pH 10) [18,19] and has been already applied to the determination of nitrite and nitrate in sea water ($ca.$ pH 8) [11]. The elution order of singly charged anions on the Capcellpak C$_{18}$ was identical to that on TSKgel IC-Anion-PW [3,4]. A longer retention volume of SCN$^-$ with lower hydration energy on Capcellpak C$_{18}$ may be due to matrix effects such as carbon-chain length on quaternary ammonium groups and surface properties.
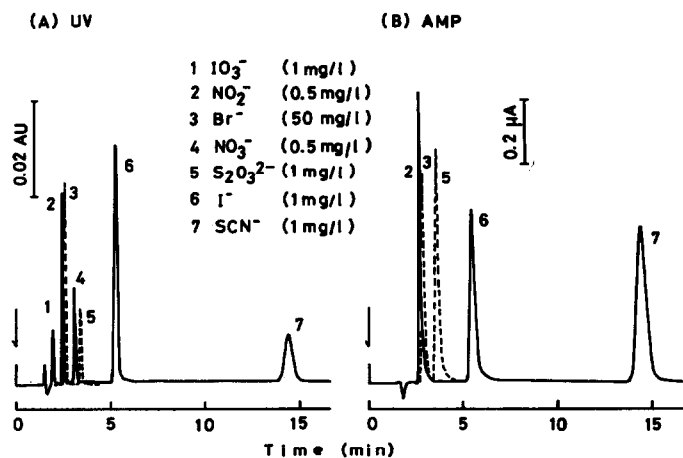

(A) UV   **(B) AMP**

1 IO$_3^-$ (1 mg/l)
2 NO$_2^-$ (0.5 mg/l)
3 Br$^-$ (50 mg/l)
4 NO$_3^-$ (0.5 mg/l)
5 S$_2$O$_3^{2-}$ (1 mg/l)
6 I$^-$ (1 mg/l)
7 SCN$^-$ (1 mg/l)

T i m e (min)

Fig. 3. Ion chromatograms of inorganic anions. Conditions: column, Capcellpak C$_{18}$ coated with 1 mM CTA$^+$ in water–methanol (56:44%, v/v); mobile phase, 0.1 M sodium chloride–5 mM sodium phosphate buffer (pH 5.8). Detection, (A) UV = 226 nm, (B) AMP = $+$ 1.0 V ($vs.$ Ag/AgCl). Flow-rate, 1.0 ml/min. Sample volume, 100 μl.
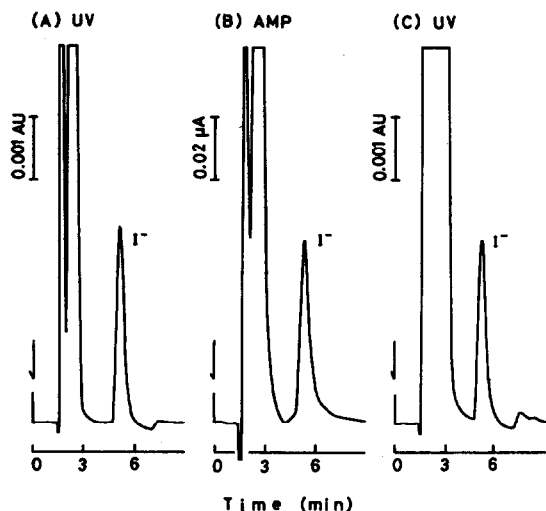
Fig. 4. Ion chromatograms of iodide (0.2 mg/l) in artificial sea water (salinity 35‰). (A) UV = 226 nm; (B) AMP = +1.0 V; (C) UV = 226 nm (iodate was reduced to iodide). Other conditions were the same as in Fig. 3.

Detection of iodine species in artificial sea water

Detection of trace-level iodine species in solutions containing an excess of salts was examined. Fig. 4A and B show ion chromatograms of iodide (0.2 mg/l) in artificial sea water (salinity 35‰) by UV and AMP methods, respectively. A good iodide peak was obtained without interference by an excess of anions; $Cl^- = 17 300$ mg/l, $SO_4^{2-} = 2710$ mg/l, $HCO_3^- = 142$ mg/l and $Br^- = 67$ mg/l.

However, the iodate peak was masked by the coexisting ions. Therefore, the optimum condition for reduction of iodate to iodide was examined by the addition of ascorbic acid and acetic acid [17] in 35‰ artificial sea water. Ascorbic acid, $2 \cdot 10^{-4}$ M, and 0.03 M acetic acid in the solution were appropriate for the completion of the reaction. Fig. 4C shows an ion chromatogram with UV detection of 0.2 mg/l IO_3^- in the artificial sea water under the reaction conditions. A good iodide peak, which was a little broad compared with Fig. 4A, was obtained. However, the peak could not be obtained by using TSKgel IC-Anion-PW, because of interference by the reductants. In the course of experiment, by the way, it was necessary to remove an AMP detector from the chromatographic system because the detector strongly responded to the reductants.

The peak heights of iodide (0.2 mg/l) in salinity 35‰ with the UV and AMP detection decreased to 45 and 50% of those in pure water, respectively. The broadness of iodide peak may be due to the self-elution of this solution and a reduction in self-diffusion of iodide in the salt solution. However, the peak areas were almost constant for eight solutions (salinity 0–45‰); the relative standard deviation (R.S.D.) was 3.8 and 3.6% with UV and AMP detection, respectively.

The calibration graphs obtained by the peak-area method for iodide (0.01–0.2 mg/l) in 35‰ artificial sea water showed downward curvatures for both methods of detection. Similar curvature was obtained in the artificial sea water containing reduc-
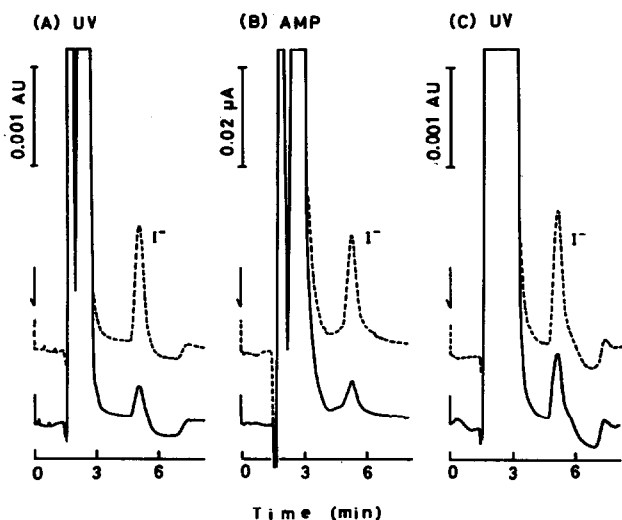
Fig. 5. Ion chromatograms of a sea water sample (Table II, No. 1). Solid lines, a real sample; dashed lines, the sample spiked with 0.05 mg/l I⁻ (A and B) and IO_3^- (C). (A) UV = 226 nm; (B) AMP = +1.0 V; (C) UV = 226 nm (iodate was converted to iodide). Other conditions were the same as in Fig. 3.

tants. The addition of salinity in samples was effective for the stability of baseline and reduction of peak noise. The detection limits (signal-to-noise ratio = 2) were 5 and 5 μg/l for iodide by the UV and AMP methods, respectively, and 10 μg/l for iodide (reduced from iodate) by the UV method. Thus, good reproducibility of ten replicate injections of 0.2 and 0.05 mg/l I⁻ in artificial sea water was obtained: the R.S.D. was 0.7% (0.2 mg/l) and 2.5% (0.05 mg/l) for UV detection, and 0.6% (0.2 mg/l) and 2.2% (0.05 mg/l) for AMP detection. For I⁻ (from IO_3^-) by the UV method, the R.S.D. was 0.9% (0.2 mg/l) and 2.3% (0.05 mg/l).

TABLE II

ANALYTICAL RESULTS OF I⁻ AND I⁻ + IO_3^- IN SEA WATER BY UV AND AMP DETECTION

Sample No. (Seto Inland Sea)	n	I⁻: UV (AMP)			I⁻ + IO_3^-: UV		
		Added (mg/l)	Found (mg/l)	Recovery (%)	Added (mg/l)	Found (mg/l)	Recovery (%)
1	4	—	0.021 ± 0.003	—	—	0.051 ± 0.004	—
		(−)	(0.017 ± 0.004)	(−)	0.050	0.102 ± 0.003	102
		0.050	0.070 ± 0.005	98			
		(0.050)	(0.068 ± 0.003)	(102)			
2	4	—	0.025 ± 0.002	—	—	0.052 ± 0.002	—
		(−)	(0.023 ± 0.004)	(−)	0.050	0.101 ± 0.007	98
		0.050	0.078 ± 0.003	106			
		(0.050)	(0.072 ± 0.004)	(98)			

Application to iodine species in sea waters

Fig. 5 shows the ion chromatograms of a sea water sample (solid line) and the sample spiked with 0.05 mg/l I^- (Fig. 5A and B) and 0.05 mg/l IO_3^- (Fig. 5C) (dashed line). The chromatograms were in good agreement with those of artificial sea water in Fig. 4. The results obtained are summarized in Table II. Good agreement between the UV and AMP methods was obtained. Moreover, quantitative recoveries were obtained.

CONCLUSION

C_{18} reversed-phase columns coated with cetyltrimethylammonium, which have a low capacity, and a sodium chloride mobile phase were found to be effective for iodide separation as an alternative to a conventional IC column system. Dissolution of sorbed CTA^+ was not observed. A good iodide peak in sea water was obtained. Further, the columns may enable the detection of iodide and thiocyanate in concentrated salt solutions.

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