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Journal of Chromatography A, 664 (1994) 117–122

JOURNAL OF  
CHROMATOGRAPHY A

### Short Communication

# Effect of functional groups on the retention behaviour of anions in ion chromatography using a coated silica column

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(First received October 19th, 1993; revised manuscript received December 28th, 1993)

## Abstract

The effect of functional groups on the retention behaviour of some anions was investigated in ion chromatography using ODS columns coated with several quaternary ammonium or phosphonium salts that have various free alkyl groups on the nitrogen and phosphorus atoms. The retention behaviour of strongly retained monovalent anions, such as nitrate and bromide, was greatly affected by the alkyl groups. However, those of divalent and weakly retained monovalent anions were little affected. The retention of anions on the quaternary phosphorus atom were stronger than those on the quaternary nitrogen atom.

## 1. Introduction

Ion chromatography has become a popular technique for the determination of anions, which is usually difficult by classical techniques [1]. It has been reported based on chemical ion-exchange selectivities that variation of the resin matrix should have a large effect on the relative selectivities of different ions [2]. Some studies on the retention behaviour of ions on the functional groups of ion-exchange resins by ion chromatography have been reported [1–5]. In some studies [3,4] functional groups reacted with styrene–divinylbenzene copolymer (XAD-1) and quaternary ammonium salts were used, and in others [2,5] XAD-1 columns coated with quaternary ammonium salts were used. The effects of alkyl

functional groups on the quaternary nitrogen atom was investigated by the use of chemically bonded trialkylammonium resins or other quaternary ammonium resins [1,3,4]. The retention of polarizable anions ( $\text{NO}_3^-$ ,  $\text{I}^-$ , etc.) was stronger than that of the other anions and increased with increasing R groups on the nitrogen atom. This was explained by the phenomenon of “water structure induced by ion pairing” [1,3].

Column coating techniques for anion chromatography have been reported [2,6–9]. The advantage of such techniques is the easy preparation of columns with various ion-exchange groups and capacities.

In this work, the effect of free alkyl groups on the quaternary nitrogen atom on the retention behaviour (or relative selectivities) of anions was studied by ion chromatography using ODS col-

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Table 1  
Chromatographic conditions

Separation column	Octadecylsilica (ODS) columns dynamically coated with various quaternary ammonium or phosphonium salts
Column temperature	35°C
Sample loop	100 $\mu$ l
Detection wavelength	210 nm
Flow-rate	1.0 ml min <sup>-1</sup>
Eluent	1.0 mmol l <sup>-1</sup> citrate (pH 6.5)

umns coated with several quaternary ammonium or phosphonium salts and with a citrate eluent. The local electrical densities (or basicities) on the quaternary nitrogen and phosphorus atoms in the ion-exchange process are briefly discussed.

## 2. Experimental

The ion chromatographic equipment consisted of a pump (CCPD; Tosoh, Tokyo, Japan), a variable-wavelength ultraviolet detector (UV-8011 or UV-8000; Tosoh), an injector (Rheodyne, Cotati, CA, USA), a column oven (CO-8000; Tosoh) and a pen recorder (YEW type 3066; Yokogawa, Tokyo, Japan). The operating conditions are given in Table 1.

All chemicals were of analytical-reagent grade, and deionized, distilled water, further filtered through a 0.45- $\mu$ m membrane filter, was used.

The eluent was 1 mmol l<sup>-1</sup> citrate, adjusted to pH 6.5 with dilute sodium hydroxide solution.

The eluent was degassed ultrasonically before use.

The quaternary ammonium and phosphonium salts used and their abbreviations are given in Table 2. CTBuABr was synthesized according to the following procedure, which was a modification of the procedure used by Ohki *et al.* [10]. Cetyl bromide (5 mmol), tri-*n*-butylamine (5 mmol) and methanol (5 ml) were placed in a glass tube, which was sealed under vacuum after several freeze–pump–thaw cycles. The sealed tube was heated for 8 h at 100°C and shaken intermittently. The synthesized CTBuABr was passed through a glass column packed with silica gel (Wakogel C-100; Wako, Osaka, Japan), after dissolution in 30% methanol solution. The column was washed with about 50 ml of 70% methanol and CTBuABr was obtained by evaporating the elute and washings. Other synthetic cetyltrialkylammonium salts and cetyltriphenylphosphonium salts were prepared from the corresponding cetyl halides and tri-

Table 2  
Quaternary ammonium and phosphonium salts

Abbreviation	Compound	Source
CTMABr	Cetyltrimethylammonium bromide	Commercially available
CTEABr	Cetyltriethylammonium bromide	Synthesized
CTPrABr	Cetyltripropylammonium bromide	Synthesized
CTBuABr	Cetyltributylammonium bromide	Synthesized
CPyCl	Cetylpyridinium chloride	Commercially available
CDMEABr	Cetyldimethylethylammonium bromide	Commercially available
CDMBuABr	Cetyldimethylbutylammonium bromide	Synthesized
CDMBnACl	Cetyldimethylbenzylammonium chloride	Synthesized
CTBuPBr	Cetyltributylphosphonium bromide	Commercially available
CTPhPI	Cetyltriphenylphosphonium iodide	Synthesized

alkylamines or triphenylphosphine in a procedure similar to the synthesis of CTBuABr except for the heating temperature; CTEABr 90°C, CTPrABr 100°C and CTPhPI 130°C. All of the compounds were similarly purified with silica gel. CDMBuABr and CDMBnACl were synthesized from cetyldimethylamine and *n*-butyl bromide and benzyl chloride, respectively, and similarly purified with silica gel.

Dynamically coated columns were prepared from columns (50 × 4.6 mm I.D.) packed with ODS resin (Capcell Pak C<sub>18</sub>, AG-120, 5 μm particle size; Shiseido, Tokyo, Japan), which has no silanol groups. No retention of anions was observed on this ODS resin. The coating procedure was similar to that used by DuVal and Fritz [2] and Mullins [9]. The column was coated with about 70 ml of 0.01 mol l<sup>-1</sup> quaternary ammonium or phosphonium salt in about 10% methanol solution at a flow-rate of 0.5 ml min<sup>-1</sup>. The end of the coating procedure was confirmed by absorbance monitoring during elution. They were then conditioned with the eluent before testing. The column capacities were calculated from the measurement of the eluate absorbance during the eluent conditioning.

### 3. Results and discussion

The effect of trialkyl (R) groups in cetyltrialkylammonium groups (C<sub>16</sub>R<sub>3</sub>N<sup>+</sup>) on the capacity factors of some anions was examined. The results obtained are given in Table 3 and the chromatograms of some anions of CTMABr- and CTBuABr-coated columns are shown in Figs. 1 and 2, respectively. The effect of the column capacity on the retention of anions could be ignored, as almost identical column capacities were obtained, as shown in Table 3. The retention of polarizable (or strongly retained) monovalent anions, such as nitrate, nitrite and bromide, increased with the larger R groups, whereas this tendency was only slight for weakly retained monovalent anions, such as chloride, fluoride, phosphate and hydrogencarbonate. Benzoate, iodide and thiocyanate as monovalent anions were very strongly re-

tained on the coated columns and their retention behaviour could not be observed. However, the retention of divalent anions, such as oxalate, sulphate and thiosulphate, decreased with the larger R groups. A change in the elution order was also observed on these coated columns; the larger R groups reversed the elution order of nitrate and thiosulphate and of nitrite and sulphate. This retention behaviour of monovalent and divalent anions was similar to that reported by Barron and Fritz [3,4]. They explained the effect by stronger ion pairing, resulting from disruption of the water structure by the anions and by tightening of the water structure surrounding the ion pair by the larger R groups for poorly hydrated anions, such as bromide, iodide and nitrate. On the other hand, the retention of nicotinate as a monovalent anion also decreased. This may be due to the size exclusion effect for bulky nicotinate anion.

The local electrical densities (or basicities) on the nitrogen atom were decreased with the larger R groups, because the local electron supply to the nitrogen atom from the surrounding R groups was decreased with the larger R groups. Hence the retentions of polarizable anions were increased. However, those of divalent anions were decreased, because two sites of nitrogen atoms may be necessary for their retention in the ion-exchange process and the steric hindrance may be increased.

For the cetylpyridinium group with no free alkyl groups on the quaternary nitrogen atom, the retentions of anions were slightly weaker than those for CTMABr which had the smallest R groups, as shown in Table 3. This may be due to higher local electrical density on the nitrogen atom in the pyridinium ring.

However, the retentions of polarizable and weakly retained monovalent anions decreased with the larger monosubstituted R groups and those of divalent anions decreased slightly or were almost constant for cetyldimethylalkylammonium groups (C<sub>16</sub>Me<sub>2</sub>RN<sup>+</sup>), as shown in Table 3. The results for monovalent anions from dimethylalkylammonium groups showed the opposite tendency to those from trialkylammonium groups. However, the results for divalent anions

Table 3  
Capacity factors for anions on columns coated with quaternary ammonium or phosphonium groups

Anion	Capacity factor ( $k'$ )									
	CTMABr (0.15) <sup>a</sup>	CTEABr (0.14)	CTPrABr (0.14)	CTBuABr (0.17)	CPyCl (0.16)	CTBuPBr (0.11)	CTPhPI (-)	CDMEABr (0.17)	CDMBuABr (0.15)	CDMBnACI (0.18)
Benzoate	>60	>60	>60	>60	>60	>60	>60	>60	>60	>60
Bromide	11.3	11.7	13.0	13.3	8.3	24.0	28.0	7.4	7.1	16.8
Chloride	2.4	2.3	2.3	2.3	2.3	3.8	2.7	1.9	1.8	3.4
Fluoride	0.7	0.7	0.7	0.7	0.7	0.7	0.8	0.7	0.7	0.8
Hydrogen carbonate	0.7	0.7	0.7	0.7	0.7	0.7	0.8	0.7	0.7	0.8
Iodide	>60	>60	>60	>60	>60	>60	>60	>60	>60	>60
Nicotinate	13.1	-	-	4.7	11.7	5.9	-	11.1	4.6	7.0
Nitrate	19.5	21.7	31.3	41.3	12.0	55.0	65.7	13.7	12.1	25.7
Nitrite	6.0	6.7	6.7	8.0	4.0	10.0	8.5	4.2	3.7	6.6
Oxalate	7.8	-	-	3.9	7.0	6.3	10.7	-	7.6	7.9
Phosphate	1.3	1.3	1.3	0.7	1.0	1.1	0.8	-	0.9	0.8
Sulphate	6.3	4.3	3.3	3.0	5.3	4.0	2.3	5.1	4.6	6.6
Thiosulphate	25.7	19.7	13.3	13.3	19.3	30.0	16.6	-	20.7	55
Thiocyanate	>60	>60	>60	>60	>60	>60	>60	>60	>60	>60

Chromatographic conditions as in Table 1.

<sup>a</sup> Values in parentheses are ion-exchange capacities of the coated columns in mequiv. per column.

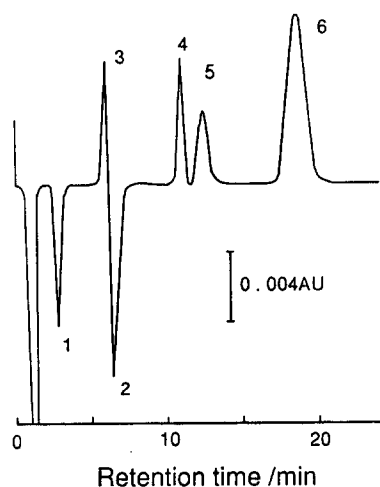


Fig. 1. Separation of anions on CTMABr-coated column. Peaks: 1 = chloride ( $10 \mu\text{g ml}^{-1}$ ); 2 = sulphate ( $40 \mu\text{g ml}^{-1}$ ); 3 = nitrate ( $1 \mu\text{g ml}^{-1}$ ); 4 = bromide ( $6 \mu\text{g ml}^{-1}$ ); 5 = nicotinate ( $60 \mu\text{g ml}^{-1}$ ); 6 = nitrate ( $4 \mu\text{g ml}^{-1}$ ). Conditions as in Table 1. Peaks as in Fig. 1.

from both groups showed similar a tendency and no change in the elution order of anions was observed. The effect of alkyl groups on the local electron supply to the nitrogen atom for dimethylalkylammonium groups is much smaller than that for trialkyl groups, and the effect of the hydrophobic mono-R groups for the retention of anions increased with the larger R groups. This was also indicated by a stronger retention of

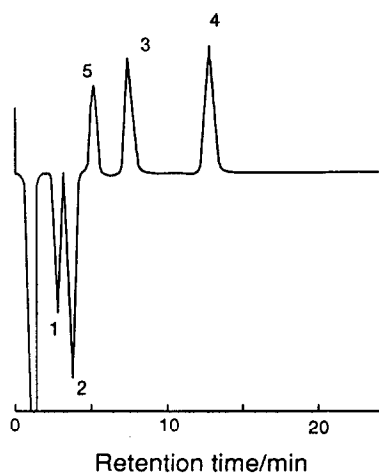


Fig. 2. Separation of anions on a CTBuABr-coated column. Conditions as in Table 1. Peaks as in Fig. 1.

anions on the CDMBnACl-coated column, as shown in Table 3.

Quaternary phosphonium groups (CTBuP<sup>+</sup> and CTPhP<sup>+</sup>) instead of quaternary ammonium groups were also examined. The retention of most anions, especially polarizable anions, increased on the CTBuPBr-coated column compared with the CTBuABr-coated column, in spite of low ion-exchange capacity on the former column, as shown in Table 3 and Figs. 1 and 3. This may be explained by the difference in electronegativities between nitrogen and phosphorus atoms.

The anions may be retained on the resins in ion chromatography by complex interactions, such as ion-exchange processes, hydrophobic interactions and the ion-pairing effect. In this paper, the retention of anions has been discussed from the point of view of the local electrical densities (or basicities) on the quaternary nitrogen atom in the ion-exchange process. The retention behaviour of polarizable (strongly retained) monovalent anions, such as nitrate and bromide, was greatly influenced by the free alkyl groups on the quaternary nitrogen atom, but that of divalent and weakly retained monovalent anions varied little. Hence the selection of functional groups also contributes to the improvement of the resolution of anions (especially monovalent and divalent anions) in ion chromatography.

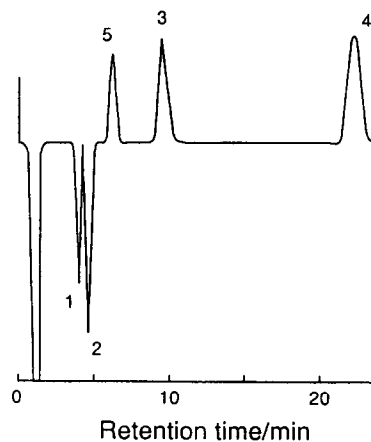


Fig. 3. Separation of anions on a CTBuPBr-coated column. Conditions as in Table 1. Peaks as in Fig. 1.

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