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Note

Effect of methanol in the mobile phase on the ion chromatographic determination of some monovalent cations

R. C. BUECHELE* and D. J. REUTTER
Research Unit, Forensic Science Research and Training Center, FBI Academy, Quantico, VA 22135 (U.S.A.)

The determination of several amines, ammonia and alkali metals by ion chromatography has been reported previously[1,2]. The moderate efficiencies still exhibited by ion-exchange columns make the determination of many of these ions impossible in the presence of other ions with similar retention times unless sample pre-treatment or other independent methods are used.

Similar difficulties in the separation of some amino acids by ion-exchange chromatography have been resolved by changing column selectivities with the addition of an organic solvent to the mobile phase[3–5]. These selectivity changes have been attributed to a combination of several retention mechanisms which can be important in chromatographic separations using ion-exchange resins. The addition of an organic solvent to the mobile phase has a significant effect on several of these mechanisms.

The application of this phenomenon to ion chromatography has received little attention. This is due, in part, to the fact that organic solvents suppress ionization and consequently decrease sensitivity with conductivity detection. Furthermore, organic solvents swell the sulfonated polystyrene–divinyl benzene resins commonly used in ion chromatography thus increasing back pressure[6,7]. We have investigated these problems and found that the advantages gained by large changes in column selectivities can outweigh the disadvantages for some analyses.

EXPERIMENTAL

Apparatus

The ion chromatograph used was a Dionex Model 16 (Dionex, Sunnyvale, CA, U.S.A.) which was equipped with a 6-μl flow-through conductivity detector. Samples were introduced by an air actuated valve injector with a 100-μl sample loop. The analog output from the conductivity detector (which is proportional to the square of the conductivity in the cell) was recorded on a Shimadzu C-RIA integrating recorder.

Columns

The analytical column was a 6 × 250 mm "cation separator" column

(Dionex). A 9 × 250 mm anion exchange suppressor column (Dionex) preceded the conductivity cell to strip the highly conductive HCl from the mobile phase.

Chemicals

Grade one deionized water (Hydro Services), Baker analyzed HPLC grade methanol and ACS certified 1 *N* hydrochloric acid (Fisher) were used to prepare the ion chromatography eluents. Sodium nitrate, ammonium nitrate, potassium nitrate, lithium carbonate and rubidium chloride (certified ACS grade, Fisher) were used to prepare the inorganic cation standards. Cesium chloride and the amines were supplied by Sigma (St. Louis, MO, U.S.A.). Each reagent was dissolved in deionized water to yield standard solutions of approximately 10 ppm (w/w) of the cation.

Mobile phases

The mobile phases consisted of 0.01 *N* hydrochloric acid in water–methanol solutions. The quantity of methanol was varied in each of the five mobile phases as follows: (a) 40 ml 1 *N* hydrochloric acid diluted to 4 l with deionized water (0% v/v, methanol); (b) 40 ml 1 *N* hydrochloric acid, 400 ml methanol, diluted to 4 l with deionized (10% v/v, methanol); (c) 40 ml 1 *N* hydrochloric acid, 800 ml methanol, diluted to 4 l with deionized water (20% v/v, methanol); (d) 40 ml 1 *N* hydrochloric acid, 1200 ml methanol, diluted to 4 l with deionized water (30% v/v, methanol); (e) 40 ml 1 *N* hydrochloric acid, 1600 ml methanol, diluted to 4 l with deionized water (40% v/v, methanol).

Procedure

Retention times for the cations shown in Table I are reported as mean values from at least three injections with a relative standard deviation of less than 2%. In all

TABLE I

RETENTION TIMES FOR MONOVALENT CATIONS USING 5 DIFFERENT MOBILE PHASES

Each mobile phase contained 0.01 *N* HCl and varied only in methanol content. Flow-rate was held constant at 1.53 ml/min.

Ion	Retention time (min)				
	Methanol (%)				
	0	10	20	30	40
Li$^+$	9.69	9.83	9.99	10.15	10.66
Na$^+$	11.36	11.52	11.89	12.27	13.67
NH$_4^+$	14.69	14.65	15.00	15.27	16.70
K$^+$	16.16	16.61	18.23	19.74	23.33
Rb$^+$	19.12	17.87	19.96	22.97	27.27
Cs$^+$	23.26	21.14	23.64	27.30	32.57
Ethanolamine	15.26	15.21	15.61	15.87	17.49
Diethanolamine	16.50	16.11	16.51	16.45	17.55
Triethanolamine	19.29	18.18	17.93	17.69	19.10
Ethylamine	18.66	17.92	17.91	18.10	19.89
Diethylamine	26.88	24.07	23.19	22.58	24.08
Triethylamine	39.66	31.68	28.15	25.95	26.92
Methylamine	16.84	16.53	16.86	17.34	19.34
Trimethylamine	23.13	21.61	21.55	21.50	23.60

cases. the flow of the mobile phase was maintained at 1.53 ml/min. The selectivity was determined by the equation:

$$\alpha = \frac{K_2}{K_1} \tag{1}$$

where K_2 is the retention time of the sample ion and K_1 is the retention time of the least retained species. (Li^+). At 40% methanol concentration the linearity was studied for selected cations to determine if addition of methanol had an adverse effect. The signal and signal-to-noise (S/N) ratios were compared at zero and 40% methanol. The signal was measured as peak height of sodium at 10 ppm, and the noise was determined as the peak-to-peak voltage of the sinusoidal variation in the baseline over a 2-min period.

RESULTS

The addition of methanol to the mobile phase of the cation ion chromatography system altered the selectivity of the separator column. For many pairs of ions the retention orders were reversed when going from 0 to 40% methanol. Table I lists retention times for all the ions studied as a function of methanol concentration in the mobile phase. Fig. 1 plots selectivity *versus* percentage methanol in the mobile phase for inorganic monovalent cations, and Fig. 2 shows the same functions for the monovalent amines which were considered.

Fig. 3 shows a graph of integrated signal as a function of the concentrations of Na^+, NH_4^+, K^+ and methylamine, over the range 1 to 50 ppm for the system containing 40% methanol. Others have reported response *vs.* concentration for these ions using eluents without organic modifiers[2]. Comparison of the peak heights of representative ions when they are run on the 0 and 40% methanol systems, indicates that at an ion concentration of 10 ppm, the 40% methanol system gives only 1/3 of the response measured in the 0% methanol system. However, when the S/N ratio is measured for Na^+ at 10 ppm as is described in the procedure. the ratio drops from
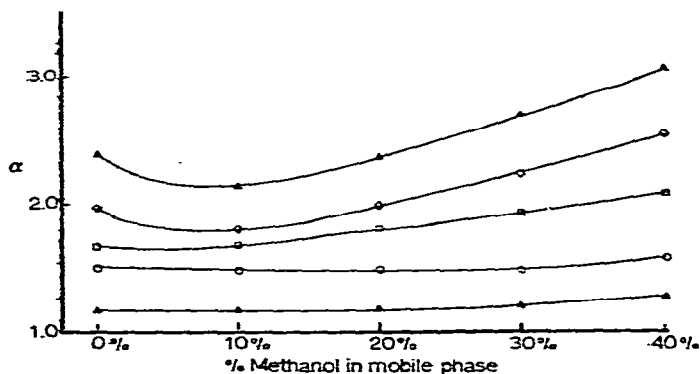

Fig. 1. Relationship between selectivity (α) and percent methanol in the mobile phase for inorganic monovalent cations. $\triangle = Na^+$, $O = NH_4^+$, $\square = K^+$, $\diamondsuit = Rb^+$, $\blacktriangle = Cs^+$.
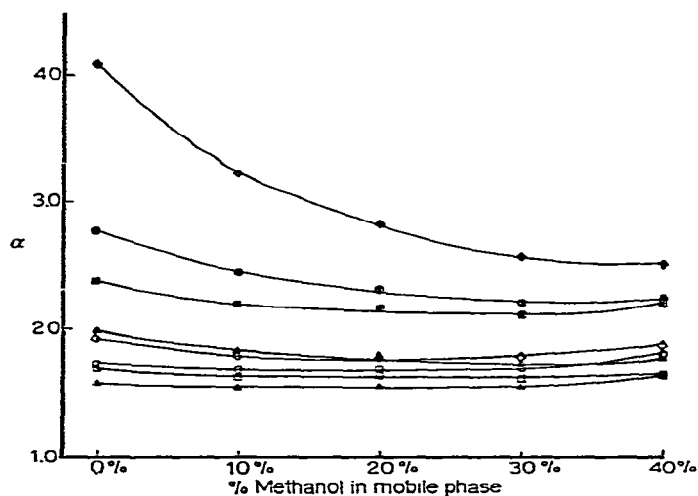
Fig. 2. Relationship between selectivity (α) and percent methanol in the mobile phase for monovalent amines. $\triangle$ = Ethanolamine, $\square$ = diethanolamine, $\bigcirc$ = methylamine, $\blacktriangle$ = triethanolamine, $\diamondsuit$ = ethylamine, $\blacklozenge$ = triethylamine, $\bullet$ = diethylamine, $\blacksquare$ = trimethylamine.
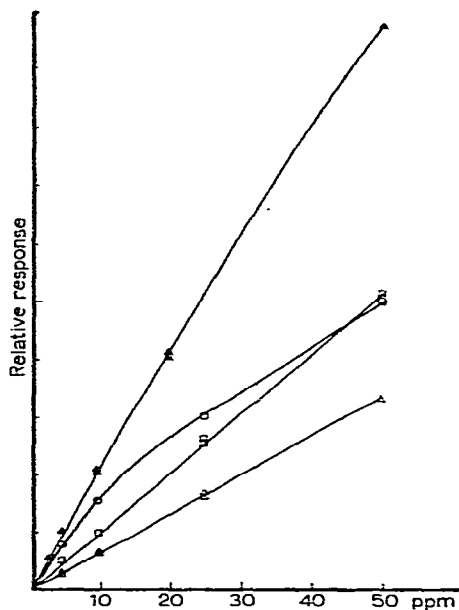

Fig. 3. Relationship between cation concentration and relative detector response for the mobile phase containing 40% methanol. $\triangle$ = K^+, $\square$ = Na^+, $\bigcirc$ = NH_4^+, $\blacktriangle$ = methylamine.

20,500 to 18,000. This is due to a significant drop in the background noise which accompanies the suppression of the signal.

DISCUSSION

The addition of methanol to the mobile phase of a cation ion chromatography

system can be used to separate ions which would not be separated by aqueous eluents. The large drop in detector response which is due to suppression of ionization by the organic solvent is not a significant detriment to the use of such solvents in ion chromatography. Even at 40 % methanol concentration, the S/N ratio is decreased by approximately 10 %; therefore, the detector output can be electronically amplified with little overall loss in performance. Moreover, an eluent containing 40 % methanol produces similar results for linearity of signal vs. ionic concentration when compared to the previous study[2].

The influence of organic solvents in the mobile phase on retention mechanisms for ion-exchange chromatography has been previously discussed[5,8]. For simplicity, we can characterize the phenomenon as one involving two separate processes, both of which are affected by the addition of the organic solvent. First, there is the interaction of the methanol with the ion-exchange resin swelling the resin and increasing the capacity by better exposing the available ion-exchange sites and increasing the area for adsorption. Second, the addition of methanol to the aqueous eluent changes the free energy of solvation for each cation. These effects are apparent upon examining Figs. 1 and 2. The alkali earths are generally more retained with the addition of methanol while the amines are generally less retained.

One application which takes advantage of these selectivity changes is the separation of potassium and methylamine. The eluent recommended by the manufacturer of the ion chromatograph (0.005–0.0075 N hydrochloric acid) will not resolve these two ions. With the addition of 40 % methanol to the mobile phase, baseline resolution is obtained. These separations are shown in Figs. 4 and 5, respectively. Other successful applications of this elution method depend upon the needs of the particular separation. Table I offers a basis for selecting an eluent which may provide workable separations for monovalent cations. Other organic solvents which are compatible with the ion-exchange resins could be equally applicable. Our studies have included only acetonitrile which yields results similar to those reported here with methanol.
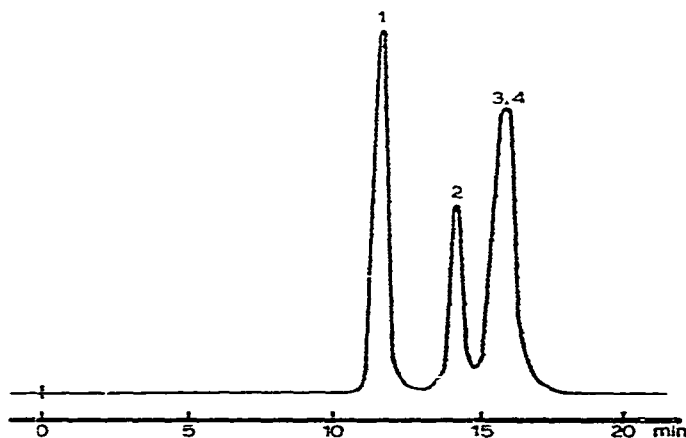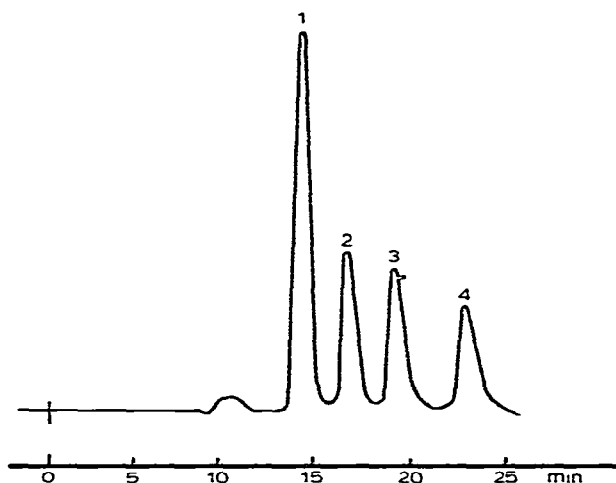

Fig. 4. Ion chromatogram of a solution containing 10 ppm each of Na^+, NH_4^+, K^+ and methylamine. Mobile phase is 0.01 N HCl in deionized water with 0 % methanol. Peaks: 1 = Na^+, 2 = NH_4^+, 3 = K^+ and 4 = methylamine.

Fig. 5. Ion chromatogram of a solution containing 10 ppm each of Na$^-$, NH$_4^+$, K$^+$ and methylamine. Mobile phase is 0.01 N HCl in deionized water with 40% methanol added. Peaks: 1 = Na$^+$, 2 = NH$_4^+$, 3 = methylamine and 4 = K$^+$.

This research has applied to a modern ion chromatography system the proven practice of changing ion-exchange column selectivities by the addition of an organic solvent to the mobile phase. This has proven useful for some of our applications and creates potential for further research in ion chromatography.

ACKNOWLEDGEMENTS

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