

Novel silica-based strong anion exchanger for single-column ion chromatography

CHING-ERH LIN*, YONG-HWA YANG and MEI-HUI YANG

Department of Chemistry, National Taiwan University, Taipei 10764 (Taiwan)

ABSTRACT

A novel silica-based anion exchanger for single-column ion chromatography was prepared by immobilizing a quaternary ammonium salt of cyanuric chloride onto the surface of silane-modified silica-gel. A stationary phase with low capacity (0.38 mequiv./g) was obtained and effective separation of monovalent anions was achieved with a concentration of tartaric acid or *o*-phthalic acid lower than 0.5 mM on a short column prepared using a conductometric detector. Factors that can affect the retention behaviour, such as eluent species, eluent concentration and eluent pH, were examined. The results demonstrate that the retention of anions is dominantly governed by ion-exchange interactions. However, the matrix effect due to the interaction between the stationary phase and the eluent may also play an important role.

INTRODUCTION

Ion chromatography provides a means for the rapid separation and determination of mixtures of inorganic and/or organic ions in aqueous media^{1–4}. In the single-column ion chromatographic method developed by Fritz and co-workers^{5–8}, a conductivity detector could be connected directly to a separation column employing a low-capacity ion-exchange material which allowed the use of a low concentration and, in most instances, a low equivalent conductance of the eluent so that the background conductivity could remain low. Nevertheless, eluents with high equivalent conductivity, such as potassium hydroxide, could also be used occasionally^{9–11}. Further, the eluents so chosen should have a sufficiently high affinity for the ion-exchange material that the eluent anions can compete with the sample anions for the active sites on the ion-exchange surface and move the sample anions through the column.

In an attempt to design an ion-exchange material specifically for anion chromatography, Fritz and co-workers^{5,6,12} synthesized a range of low-capacity anion-exchange resins. These surface-aminated macroporous ion-exchange resins do not provide adequate column efficiency for most applications because of the large particle size. In view of this, efforts have been directed towards the design of new high-efficiency resin-based ion exchangers with low ion-exchange capacities and small particle size¹³.

Concurrent with the development of the resin-based ion exchangers, silica-based materials, which have better mechanical strength and do not swell in organic eluents, were also developed for anion chromatography. The silica-based anion exchangers were produced by bonding quaternary ammonium functions onto microparticle silica with low capacity (0.1–0.3 mequiv./g)^{14,15}. The main drawback of the silica-based columns is that their operating pH range is limited to 2–6 owing to the dissolution problem of hydroxyl-ion attack¹⁶, and this in turn restricts both the range of sample loadings and the choice of eluents that can be used³. Also, on some occasions the occurrence of system peaks in single-column ion chromatography may cause detection problems^{17–19}. However, the commercial availability of silica-based columns, which show relatively high efficiencies^{3,20}, has led to the development of a considerable number of specialized applications⁴.

In this investigation, an attempt was made to seek an alternative route to the synthesis of a silica-based strong anion exchanger. A new low-capacity anion exchanger was prepared by immobilizing a quaternary ammonium salt of cyanuric chloride onto the surface of a silane-modified silica gel. A short column was used so that the column void volume and subsequent run time could be reduced. Factors such as eluent species, eluent concentration and eluent pH, all of which may affect the retention behaviour of anions, were investigated using a conductometric detector. The results of this work may provide a useful new route to the synthesis of silica-based strong anion exchangers so that highly efficient and effective chromatographic separations can be achieved. Further, the introduction of the moiety of the trifunctional *s*-triazine ring to the spacer arm of the stationary phase can be further modified so that difficulties encountered with currently available silica-based anion exchangers can be minimized.

EXPERIMENTAL

Chemicals

Triethylamine and cyanuric chloride were obtained from Riedel-de Haën (Hannover, F.R.G.). The silica gel used was LiChrosorb SI 60 (particle size, 10 μm ; pore size, 6 nm) obtained from E. Merck (Darmstadt, F.R.G.). Tartaric acid was purchased from J. T. Baker (Phillipsburgh, NJ, U.S.A.), *o*-phthalic acid from Wako (Osaka, Japan) and 3-aminopropyltriethoxysilane (APS) from Petrarch Systems (Bristol, PA, U.S.A.). Other synthesis reagents for the preparation of anion exchanger were of the highest available purity. Water was purified by ion exchange followed by a Milli-Q water purification system (Millipore, Bedford, MA, U.S.A.).

Preparation of silica-based anion exchanger

Quaternary ammonium salt of cyanuric chloride. A solution of 0.02 mol of cyanuric chloride in 30 ml of acetone was added with agitation to a 300-ml beaker containing 20 ml of acetone and 40 ml of water in an ice-bath at *ca.* 5°C, followed by dropwise addition of 2.8 ml (0.02 mol) of triethylamine. The mixed solution was reacted for 30 min. The white product was precipitated and filtered off, washed well with acetone and then dried at reduced pressure. The melting point of the product was higher than 300°C.

Silane-modified silica gel. Silica gel (3 g) dried at 150°C *in vacuo* for 18 h was

suspended in 150 ml of dry toluene, then 1.0 ml of 3-aminopropyltriethoxysilane was added. The reaction mixture was refluxed under nitrogen for 12 h with stirring. The silane-modified silica gel thus obtained was filtered, washed thoroughly with toluene, methanol and acetone successively (or Soxhlet extracted with methanol after washing with toluene), then dried in an oven at 70°C for 4 h.

Silica-based strong anion exchanger. Silane-modified silica gel (3 g) was suspended in a mixture of 100 ml water and 50 ml of acetone to which 0.88 g of the quaternary ammonium salt of cyanuric chloride was added. A solution of sodium hydrogencarbonate was slowly added to this suspension with agitation. While keeping the reaction temperature at 38°C, the reaction was terminated after 24 h and the product was filtered off, washed thoroughly with water, methanol and acetone successively, and then dried over P₂O₅ at reduced pressure for 8 h. The reaction scheme for the preparation of the anion exchanger is shown in Fig. 1. As can be seen, the moiety of the *s*-triazine ring is covalently bonded to the amino group of the silane-modified silica surface.

Elemental analyses of the strong anion exchangers were carried out. The average nitrogen and carbon contents obtained in three separate experiments were $2.71 \pm 0.05\%$ and $5.66 \pm 0.01\%$, respectively. The anion-exchange capacity determined from the average nitrogen percentage obtained by elemental analysis was 0.38 mequiv./g. The ion-exchange capacity (*I*) was calculated using the equation I (mequiv./g) = $[N(\%) \cdot 1000] / (5 \cdot 14 \cdot 100)$.

Standard solutions and eluent

Stock standard solutions of 1000 ppm of the various anions were prepared from analytical-reagent grade reagents with doubly deionized water. Potassium salts were used in all instances. Working standard solutions were obtained by diluting the stock standard solutions with deionized water. Eluents were prepared by dissolving the acid in water and, if necessary, adjusting the pH with 1 M potassium hydroxide solution. The eluents used were filtered through a 0.45- μ m membrane filter and degassed by ultrasonic vibration prior to use.

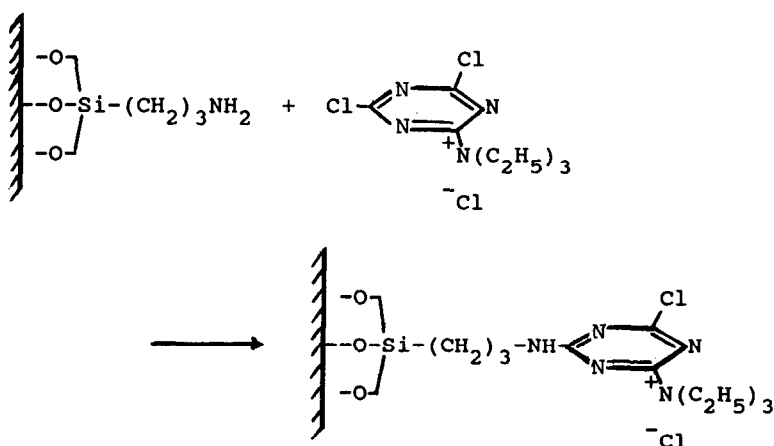


Fig. 1. Reaction scheme for the preparation of the strong anion exchanger.

Apparatus and chromatography

All ion chromatographic studies were carried out with an ion chromatographic system which consisted of a Waters Assoc. Model 510 solvent-delivery system, a U6K universal injector and a Toyo Soda Model CM-8000 conductivity detector. The integrator used was a Waters Assoc. Model 740 data module. A stainless-steel column (50 × 4 mm I.D.) was packed with isopropanol as the slurry solvent using a Chemco Model C_{pp-085} slurry-packing apparatus (Chemco Scientific, Japan) at about 350 kg/cm². The range of the conductometric detector was set at 0.005 and the gain at 50. The conductivity cell was maintained at 35°C. The flow-rate of the eluent was kept at 1 ml/min. The elemental analyses were carried out with a Perkin-Elmer Model 240C elemental analyser.

RESULT AND DISCUSSION

As the eluent anions compete with the sample anions during the chromatographic process, changes to the eluent species, eluent concentration and/or eluent pH, which may affect the retention behaviour of the sample anions, were investigated so that the retention process of the column prepared in this study could be characterized.

Effects of eluent species and eluent concentration

In order to separate the sample anions effectively, the eluent anion must be sufficiently attracted to the ion-exchange material that a very low concentration of the eluent will move sample anions to be separated through the column. However, the conductance of the eluent must also be low so that the background conductivity can remain low. As organic acids tend to have a low equivalent conductance and a wide range of p*K*_a values, which allow a great degree of flexibility in tailoring retention as a function of pH, organic acids and their salts are the most common eluents for anion analysis in single-column ion chromatography^{4-6,21,22}. In this investigation, tartaric acid and *o*-phthalic acid were among the eluents found to be successful.

To elucidate the role of ion-exchange interactions, chromatographic data that can define the influence of eluent concentration on retention at constant pH are needed. Table I gives the adjusted retention times of some common anions detected using tartaric acid and *o*-phthalic acid as the eluents at various concentrations, while maintaining the eluent pH at 4.0. The adjusted retention time of a solute anion (*t*'_R) is defined as $t'_R = t_R - t_0$, where *t*_R is the retention time of the solute anion and *t*₀ is the retention time of the injection peak. The interaction of the anion exchanger with the eluent anions appears to be electrostatic because an increase in eluent concentration causes a decrease in retention time, as can be seen in Table I. This is due to the increased ionic strength of the eluent. Hence the expected trend in retention as the eluent concentration is varied is clearly evident^{4,18,21,23,24}. As the ion-exchange process is largely governed by electrostatic interactions, the retention is thought to be the result of the strength of this interaction, especially for inorganic anions.

As is also indicated in Table I, better separations could be achieved at eluent concentrations lower than 0.5 mM and the retention times of the anions were found to be longer with tartaric acid than with *o*-phthalic acid at the same concentration and pH. Therefore, tartaric acid should be a more effective eluent and the chromatographic performance of the separation of anions on the column prepared was significantly

TABLE I

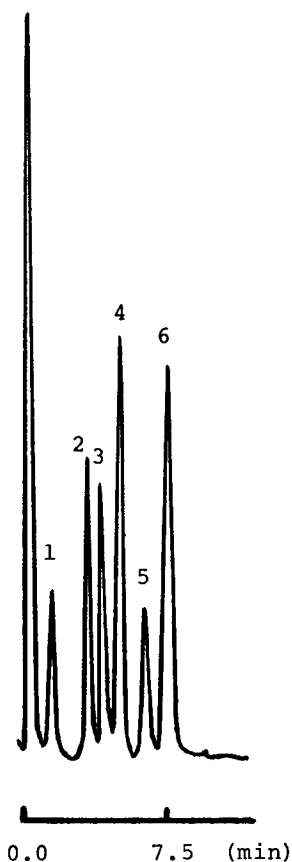
ADJUSTED RETENTION TIMES OF ANIONS USING ORGANIC ACIDS AS THE ELUENT AT VARIOUS CONCENTRATIONS

Column, 50 × 4.6 mm I.D. (0.38 mequiv./g); eluent pH, 4.0; flow-rate, 1 ml/min.

Anion	Adjusted retention time (min)					
	Tartaric acid (mM)			<i>o</i> -Phthalic acid (mM)		
	0.1	0.25	0.5	0.1	0.25	0.5
IO ₃ ⁻	4.61	3.25	2.31	4.04	2.57	2.00
Cl ⁻	4.81	3.34	2.27	3.96	2.54	1.85
BrO ₃ ⁻	4.97	3.55	2.41			
Br ⁻	5.23	3.69	2.57	4.35	2.65	2.02
NO ₂ ⁻	5.58	4.00	2.84	4.79	3.04	2.38
ClO ₃ ⁻	5.69	4.21	2.80	4.74	3.02	2.11
NO ₃ ⁻	6.73	4.92	3.34	5.62	3.59	2.73
I ⁻	6.86	5.02	3.41	5.46	3.53	2.71
ClO ₄ ⁻	8.77	6.35	4.36			
SCN ⁻	10.2	7.42	5.03	7.83	4.80	3.71
Formate	5.28	3.91	2.80	4.75	3.23	2.44
Acetate	1.77	1.40	1.08	1.49	1.18	0.09
Propionate	1.95	1.62	1.19	1.59	1.28	1.05

improved when tartaric acid, instead of *o*-phthalic acid, was chosen as the eluent. The elution order of some common anions with tartaric acid at pH 4.0 was acetate < propionate < IO₃⁻ ≤ Cl⁻ < BrO₃⁻ < Br⁻ < formate < NO₂⁻ ≤ ClO₃⁻ < NO₃⁻ ≤ I⁻ < ClO₄⁻ < SCN⁻. A typical chromatogram for the separation of acetate, Cl⁻, NO₂⁻, NO₃⁻, ClO₄⁻ and SCN⁻ anions on a short column (50 × 4.6 mm I.D., 0.38 mequiv./g) using 0.25 mM tartaric acid as the eluent at pH 4.0 is shown in Fig. 2. Thus, anions such as NO₂⁻ (or ClO₃⁻), NO₃⁻ (or I⁻) and ClO₄⁻ can be effectively separated between Cl⁻ and SCN⁻. On the other hand, the elution order was acetate < propionate < Cl⁻ ≤ IO₃⁻ < Br⁻ < ClO₃⁻ ≤ NO₂⁻ < formate < I⁻ ≤ NO₃⁻ < SCN⁻ when using *o*-phthalic acid as the eluent at pH 4.0. Reversal of the elution order was observed for some closely eluted anions, such as IO₃⁻ and Cl⁻, NO₂⁻ and ClO₃⁻, and NO₃⁻ and I⁻ when the eluent was changed from tartaric acid to *o*-phthalic acid. This observation is not unexpected because the interactions involved in the retention of solute anions for a particular stationary phase may be different with different eluent anions. This interaction, which depends on the nature of the stationary phase and the nature of the eluent anion, influences the distribution coefficient of a solute anion and can affect the competition between the eluent anion and the sample anion for the active sites on the ion-exchange material. Therefore, the retention (or the selectivity) of an anion may vary when using different eluent anions.

The data in Table I clearly indicate that the retention times of solute anions decrease considerably when using *o*-phthalic acid instead of tartaric acid as the eluent under the same conditions. Apparently, the affinity of *o*-phthalic acid for the stationary phase is greater than that of tartaric acid. The decrease in the retention times cannot be accounted for by consideration of charge effects alone, because the fraction



Retention Time

Fig. 2. Typical chromatogram for the separation of some common anions: 1 = acetate, 10 ppm; 2 = Cl^- , 3 ppm; 3 = NO_2^- , 3 ppm; 4 = NO_3^- , 5 ppm; 5 = ClO_4^- , 5 ppm; 6 = SCN^- , 10 ppm. Elution conditions: eluent, 0.25 mM tartaric acid; eluent pH, 4.0; flow-rate, 1 ml/min.

of *o*-phthalic acid existing as the divalent ion in the eluent solution is much smaller than that of tartaric acid at pH 4.0. We speculate that, apart from charge effects, matrix effects due to the adsorption of *o*-phthalic acid on the surface of the stationary phase and/or the interaction of *o*-phthalic acid with the *s*-triazine ring of the stationary phase may contribute significantly to the retention of solute anions. Indeed, it has been shown that the introduction of an *s*-triazine ring into the stationary phase can greatly affect the retention of aromatic compounds in HPLC^{25,26}.

The linear relationship between $\log t'_R$ and $\log [\text{eluent}]$ was tested for a number of anions using various concentrations of tartaric acid and *o*-phthalic acid at pH 4.0. The plots in Fig. 3 show the straight lines obtained. However, the slopes of these plots were found to deviate considerably from unity. In fact, the slopes obtained for inorganic anions, formate ion and low carboxylate ions are about 0.45, 0.39 and 0.31, respectively, when using tartaric acid as the eluent, whereas they are about 0.46, 0.41

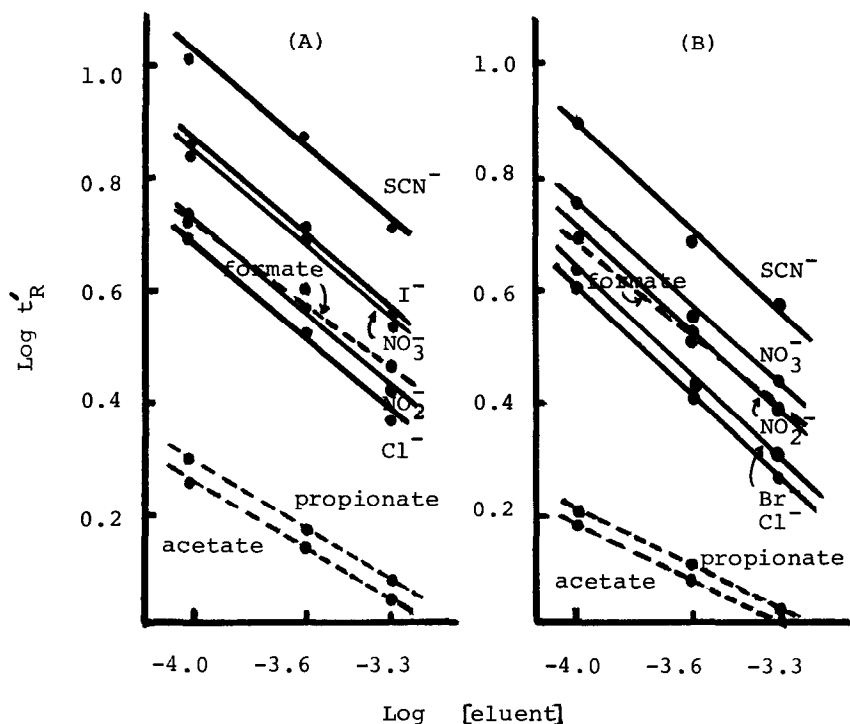


Fig. 3. Plots of $\log t'_R$ versus $\log [\text{eluent}]$ for some representative anions at pH 4.0 using (A) tartaric acid and (B) *o*-phthalic acid as the eluent. Solid lines, inorganic anions; broken lines, organic anions.

and 0.37, respectively, with *o*-phthalic acid. A similar phenomenon was observed for the hydrogencarbonate ion²⁷. At the present stage of the investigation, it is not clear why the slopes are so low. However, it may imply that the charge effect is not the only contributing factor and that the matrix effect, which depends on the nature of the stationary phase, may play an important role in the retention mechanism. Perhaps other factors such as adsorption, hydrophobic interactions between the stationary phase and the eluent and acid strength should be taken into consideration in order to account for the deviation of the slope from unity^{4,23,28}.

It is of interest that SCN^- can be effectively eluted within a reasonably short time on this column. For instance, SCN^- was eluted in 7.83 min with 0.1 mM *o*-phthalic acid at pH 4.0, whereas it had a retention time of 10.2 min at a concentration of 0.1 mM when using tartaric acid at the same pH.

Effect of eluent pH

The elution times of anions can be greatly affected by the eluent pH because the elution power increases substantially with increasing eluent pH^{4,20,21}. For example, for *o*-phthalic acid (or tartaric acid) as the eluent, the eluting power diminished when the eluent pH was above 6 (or 5). Depending on the eluent pH, some of the eluent anions are converted either into anions of lower charge or into a molecular acid^{21,24}. Table II shows the effect of eluent pH on the retention of some typical anions such as

TABLE II

ADJUSTED RETENTION TIMES OF ANIONS USING ORGANIC ACID AS THE ELUENT AT DIFFERENT pH

Column, 50 × 4.6 mm I.D. (0.38 mequiv./g); eluent concentration, 0.1 mM; flow-rate, 1 ml/min.

Anion	Adjusted retention time (min)					
	Tartaric acid (pH)			o-Phthalic acid (pH)		
	4.0	4.5	5.0	4.0	4.5	5.0
IO ₃ ⁻	4.61	2.50		4.04	2.46	1.28
Cl ⁻	4.81	2.49	1.09	3.96	2.61	1.49
BrO ₃ ⁻	4.97	2.56	1.33	4.05	2.64	1.53
Br ⁻	5.23	2.66	1.23	4.35	2.93	1.61
NO ₂ ⁻	5.58	3.17	1.58	4.79	3.11	1.75
NO ₃ ⁻	6.73	3.45	1.63	5.62	3.47	1.92
I ⁻	6.86	3.63	1.62	5.46	3.99	2.29
ClO ₄ ⁻	8.77	4.42	2.03	6.95	4.86	2.46
SCN ⁻	10.2	5.18	2.45	7.83	5.59	2.88
Formate	5.28	3.62	2.13	4.75	0.51	
Acetate	1.77	1.93		1.49	2.08	1.71
Propionate	1.95	2.11		1.59	2.42	2.23

acetate, Cl⁻, Br⁻, NO₂⁻, NO₃⁻, I⁻, ClO₄⁻ and SCN⁻ using tartaric acid or *o*-phthalic acid as the eluent. As expected, inorganic anions could be retained longer in the column when the eluent pH was decreased. Therefore, the separation of monovalent anions becomes progressively more favourable as the eluent pH decreases.

It should be noted that the retention of organic anions behaves differently from that of inorganic anions. Although the retention time of formate ion decreases with increasing eluent pH, its retention behaviour is different from that of most of the inorganic anions and other low carboxylate ions. Acetate and propionate ions are weakly retained by the column and elute early, but their retention behaviours depend on the eluent concentration and pH. For instance, with 0.5 mM *o*-phthalic acid as the eluent, the retention increases linearly with increasing eluent pH from 3.5 to 5.0, but with 0.1 mM *o*-phthalic acid, the retention first increases from pH 4.0 to 4.5, then decreases from pH 4.5 to 5.0. A plausible explanation of this behaviour can be made in terms of the effect of pH on the nature of the surface of the stationary phase, because the ionic nature of the silica surface increases slightly with increase in eluent pH from 2 to 6, and the effect on the protonation of eluent anions and organic acid anions at low eluent pH²⁸. Nevertheless, the nature of the competition between the eluent anions and organic anions for the active sites of ion exchange becomes very complicated. Further study is needed in order to obtain a better understanding of the retention mechanism of organic anions.

Characteristics of the column

The strong anion exchangers prepared in this work are reproducible because the elemental analysis data obtained in three separate experiments are consistent. The

average values of the nitrogen, hydrogen and carbon contents are $2.71 \pm 0.05\%$, $1.25 \pm 0.02\%$ and $5.66 \pm 0.01\%$, respectively.

The anion exchangers are stable. The column was used daily to elute sample anions for 18 h at a flow-rate of 1 ml/min for at least 2 months without any noticeable changes in the band widths or the retentions of tested sample anions.

As mentioned in the Introduction, the approach of using low-capacity silica-based anion exchangers in single-column ion chromatography has the disadvantage of a limited choice of eluents. For an effective chromatographic separation of anions with a particular stationary phase, the ranges of the eluent concentration, the eluent pH and the amount of sample loading are further restricted. As the retention (or the selectivity) of anions also depends on other factors, such as the ion-exchange capacity, the functionalities of the anion exchanger and the nature of the surface of the stationary phase, in addition to the eluent species, eluent concentration and eluent pH, direct comparison between the column prepared in this work and commercially available columns, such as Vydac 302IC or Toyo Soda TSK-GEL IEX-520, is not possible owing to a lack of detailed information. However, by comparing the retention data and the chromatograms obtained in this work with those reported in the literature^{18,20,21} using a commercially available column, we conclude that the efficiency of our column is as high as that of the commercial columns and the sensitivity is much better because much lower eluent concentrations and sample loadings are required. In support of the usefulness of our column, a Waters Assoc. IC PAK A column was used in our ion chromatographic system, and it was found that much larger amounts of sample were needed in order to have detectable signals, much longer retention times were observed and the resolution was not as good as with our column. For instance, with 0.25 mM tartaric acid as the eluent at pH 4.0 and at a flow-rate of 1 ml/min, iodide and thiocyanate ions were found to be retained in the column for more than 45 min, and the retention times for Cl^- , Br^- , NO_2^- and NO_3^- were 12.25, 12.27, 19.45 and 30.31 min, respectively. Therefore, the advantages of high efficiency and high sensitivity of the column prepared in this work are clearly demonstrated.

CONCLUSIONS

A new silica-based anion exchanger was successfully prepared by immobilizing a quaternary ammonium salt to cyanuric chloride onto a silane-modified silica gel for single-column ion chromatography. Effective separations of monovalent anions can be achieved with low concentrations of tartaric acid or *o*-phthalic acid as the eluents at *ca.* pH 4.0. The thiocyanate anion can be eluted within a reasonably short time on the short column prepared. Better chromatographic separations can be achieved with tartaric acid than with *o*-phthalic acid as the eluent. The retention mechanism is dominantly governed by ion-exchange interactions. However, the matrix effect due to the interaction between the stationary phase and the eluent may play an important role in the chromatographic separation of anions.

ACKNOWLEDGEMENT

The support of the National Science Council of the Republic of China is gratefully acknowledged.

REFERENCES

- 1 J. S. Fritz, D. T. Gjerde and C. Pohlandt, *Ion Chromatography*, Hüthig, New York, 1982.
- 2 F. C. Smith, Jr., and R. C. Chang, *The Practice of Ion Chromatography*, Wiley, New York, 1983.
- 3 P. R. Haddad and A. L. Heckenberg, *J. Chromatogr.*, 300 (1984) 357.
- 4 T. H. Jupille and D. T. Gjerde, *J. Chromatogr. Sci.*, 24 (1986) 427.
- 5 D. T. Gjerde, J. S. Fritz and G. Schmuckler, *J. Chromatogr.*, 186 (1979) 509.
- 6 D. T. Gjerde, G. Schmuckler and J. S. Fritz, *J. Chromatogr.*, 187 (1980) 35.
- 7 J. S. Fritz, D. T. Gjerde and R. M. Becker, *Anal. Chem.*, 52 (1980) 1519.
- 8 D. T. Gjerde and J. S. Fritz, *Anal. Chem.*, 53 (1981) 2324.
- 9 T. Okada and T. Kuwamoto, *Anal. Chem.*, 55 (1983) 1001.
- 10 N. Hirayama and T. Kuwamoto, *J. Chromatogr.*, 447 (1988) 323.
- 11 T. Okada and T. Kuwamoto, *Anal. Chem.*, 57 (1985) 829.
- 12 R. E. Baron and J. S. Fritz, *J. Chromatogr.*, 284 (1984) 13.
- 13 R. W. Siergiej and N. D. Danielson, *J. Chromatogr. Sci.*, 21 (1983) 362.
- 14 J. E. Girard and J. A. Glatz, *Am. Lab.*, 13 (1981) 26.
- 15 R. L. Stevenson and K. Harrison, *Am. Lab.*, 13 (1981) 76.
- 16 R. W. Stout, S. I. Sivakoff, R. D. Ricker, H. C. Palmer, M. A. Jackson and T. J. Odiorne, *J. Chromatogr.*, 352 (1986) 381.
- 17 P. E. Jackson and P. R. Haddad, *J. Chromatogr.*, 346 (1985) 125.
- 18 P. R. Haddad and A. L. Heckenberg, *J. Chromatogr.*, 252 (1982) 177.
- 19 T. Okada and T. Kuwamoto, *Anal. Chem.*, 56 (1984) 2073.
- 20 S. Matsushita, Y. Tada, N. Baba and K. Hossako, *J. Chromatogr.*, 259 (1983) 459.
- 21 J. A. Glatz and J. E. Girard, *J. Chromatogr. Sci.*, 20 (1982) 266.
- 22 J. S. Fritz, D. L. Du Val and R. Barron, *Anal. Chem.*, 56 (1984) 1177.
- 23 G. Schmuckler, *J. Chromatogr.*, 313 (1984) 47.
- 24 P. R. Haddad and C. E. Cowie, *J. Chromatogr.*, 303 (1984) 321.
- 25 C. E. Lin, C. H. Chen, C. H. Lin, M. H. Yang and J. C. Jiang, *J. Chromatogr. Sci.*, 27 (1989) 665.
- 26 M. H. Yang, C. E. Lin and J. K. Fan, *Silicon Material Research Program (Monograph Series, No. 1)* National Science Council, Taiwan, 1986, p. 75.
- 27 J. S. Fritz, D. T. Gjerde and C. Pohlandt, *Ion Chromatography*, Hüthig, New York, 1982, p. 109.
- 28 B. A. Bidlingmeyer, J. K. del Rios and J. Korpl, *Anal. Chem.*, 54 (1982) 442.