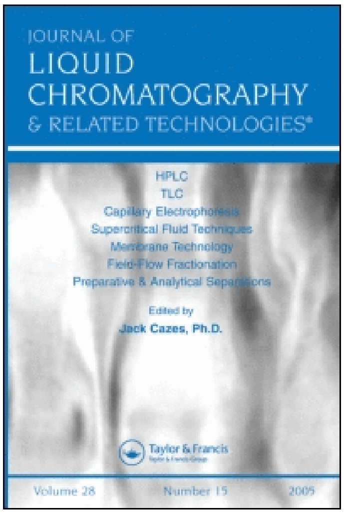

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Jimmy C. Yu[a]; Feng Qu[a]; Jun Lin[a]; HongLung Lam[a]; ZuLiang Chen[a]
[a] Department of Chemistry and the Environmental Science Programme, The Chinese University of Hong Kong, Hong Kong

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ION CHROMATOGRAPHIC SEPARATION OF ANIONS AND CATIONS ON A TITANIA PACKED COLUMN

Jimmy C. Yu,* Feng Qu, Jun Lin, HongLung Lam, and ZuLiang Chen

Department of Chemistry and the Environmental Science
Programme, The Chinese University of Hong Kong
Shatin, N. T., Hong Kong

ABSTRACT

A column packed with titania stationary phase was evaluated for the separation of ionic solutes. The retention behaviour of anions, cations and benzoic carboxylic acids were investigated using various carboxylic acids as the eleunts. Factors that strongly influenced solute retention were the type of eluent, eluent pH and concentration. The titania column exhibited significant ion exchange and ligand exchange behaviour, which depended strongly on eluent pH and types of eluents. Separation of anions, cations and simultaneous separation of anions and cations could be obtained by careful selection of the conditions of the eluent.

INTRODUCTION

Silica and resin ion exchangers are the most commonly used stationary phases for ion chromatographic (IC) separation because of their rapid mass transfer and high separation efficiency (1–3). However, a number of serious drawbacks exist with the use of silica-based IC materials. The first of these is the restricted pH range of 2–8. At pH values below 2.0, the covalent bond linking the ion-exchange functional groups are cleaved (2). Alkaline pH should also be avoided because of dissolution of the silica matrix itself. Secondly, metal ions such as Cu^{2+}, Pb^{2+} and Zn^{2+} are retained on silica ion exchangers and hence may cause interference with anions (3).

Resins are frequently used for ion chromatography since they can withstand extremes of pH. However, one significant drawback of the use of polymeric resins as ion exchangers is that they are often subject to pressure limitations. In addition, most polymers do not possess the high mechanical strength of silica and some are susceptible to swelling and contraction as the organic modifier in mobile phase changes (4–8).

Several approaches have been developed to overcome these drawbacks of silica and resin ion-exchange materials. Ceramic oxides such as alumina (9–10), zirconia (11–12) and titania (13–15) are probably the most promising materials due to resistance hydrolytic stability and high mechanical strength. Despite ceramic oxides have shown that favourable ion exchange characteristic (16). However, the use of such chromatographic packing materials for applications in HPLC has recently been developed. For example, alumina has been used as both anion and cation exchanger for the separation of inorganic anion, carboxylic acids, amines, alkaloids and proteins (11, 17–18).

Similar results were obtained for zirconia and polybutadiene coated column have been evaluated as chromatographic packing for the separation of various polar and non-polar solutes such as polycyclic aromatic hydrocarbons, nucleotide and proteins (19–21).

Titania has recently received attention as a chromatographic packing material. It exhibits anion exchange characteristic at acidic pH and cation exchange characteristic at alkaline pH (16). A number of studies have shown enhanced chemical and mechanical stability using this alternative support (22–28). Tani et al. (22–23) recently reported that the titania synthesised in their laboratory were useful as a packing material for ion chromatographic separation of anions and cations when acetate or bicine buffers used.

This result demonstrates that titania used as packing material, has the ion-exchange characteristics necessary for the simultaneous separation of anion and cation. In later work, titania packed columns were employed for the separation of carboxylic acids using bicine buffer of pH 8.7. It was found that the titania column exhibited the ligand exchange characteristics attributed to the formation of chelate ring (25). However, it is necessary to systematically investigate the retention behaviour of ionic solutes on titania columns using a new range of eluents in order to provide the full potential of this material to ion chromatography.

An octadecycyl bonded titania phase has been used in reversed-phase liquid chromatography for the separation of base solute, polyaromatic hydrocarbons and arylketons (26–29). The observed chromatographic behaviour suggested typical reverse phase as evidenced by the symmetrical peak shapes obtained with the separation of these solutes (26).

In this paper, we systematically investigated the retention behaviour of inorganic anions (NO_3^-, Cl^-) and cations (Li^+, Na^+, NH_4^+ and K^+) on titania packed column using carboxylic acidic eluents to examine ion- and ligand- exchange characteristics. We studied (1) the retention of anions with various carboxylic eluents, (2) the retention of cations using carboxylic elunts, and (3) the simultaneous separation of anions and cations, as well as the separation of benzonic carboxylic acid to examine the effect of ligand exchange.

EXPERIMENTAL

Preparation of Packing Material

TiO_2 (Degussa P25) mixed with 10% (w/w) activated carbon was placed in deionized water and heated under stirring at 200°C for removal of water. After drying in air, the resulting mass was carefully ground using a mortar and a pestle, then calcined in air at 520°C for four and half hours. After cooling to room temperature, the product was sieved through 170 mesh.

The material passed the sieve was washed three times with a 15 mM NaOH solution, then by deionized water many times until the upper solution appeared clear. This would remove NaOH and the smaller titania particles. The final product was dried overnight at 100°C. The prepared titania surface was examined using a Cambridge Stereoscan 360 scanning electron microscope.

Chromatographic System and Scanning Electro Microscopy

Columns of 50 mm × 4.6 mm were packed by the dry method using methanol as a solvent. To keep high packing pressure, the column was flushed with deionized water at a flow rate of 4 ml/min. The operating pressure of the system at 0.5ml/min was 280 psi.

A Waters HPLC with a variable-wavelength UV detector operated at 195 nm equipped with a 100 μl sample loop, and a Dionex DX-500 chromatography with a conductivity detector were used in this study.

RESULTS AND DISCUSSION

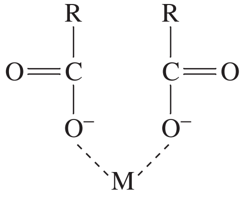
Figure 1 shows the SEM image of the titania prepared in our laboratory. It is clear that the titania is composed of particles of various size, mostly in the range of 15–25 μm. The surface of the prepared titania is estimated to be 50 m^2/g.

Since titania can retain inorganic anions and cation (16), the dominant ion- and ligand-exchange interactions are described below. This is based on the formation of an electrical double layer at the titania surface.

$$\text{M-OH} \longleftrightarrow \text{MO}^- + \text{H}^+ \text{(cation exchanger)} \qquad (1)$$

$$\text{M-OH} \longleftrightarrow \text{M}^+ + \text{OH}^- \text{(anion-exchanger)} \qquad (2)$$

$$\text{M-OH} + \text{carboxylic acid} \longleftrightarrow \qquad (3)$$



From eqns (1) and (2), the isoelectric point for titania depends both on the manner in which the titania has been treated and on the nature of the buffered used. Titania can exhibit marked anion and cation exchange characteristics in acidic and alkline media. However, eqn (3) shows that ligand exchange occurs under the

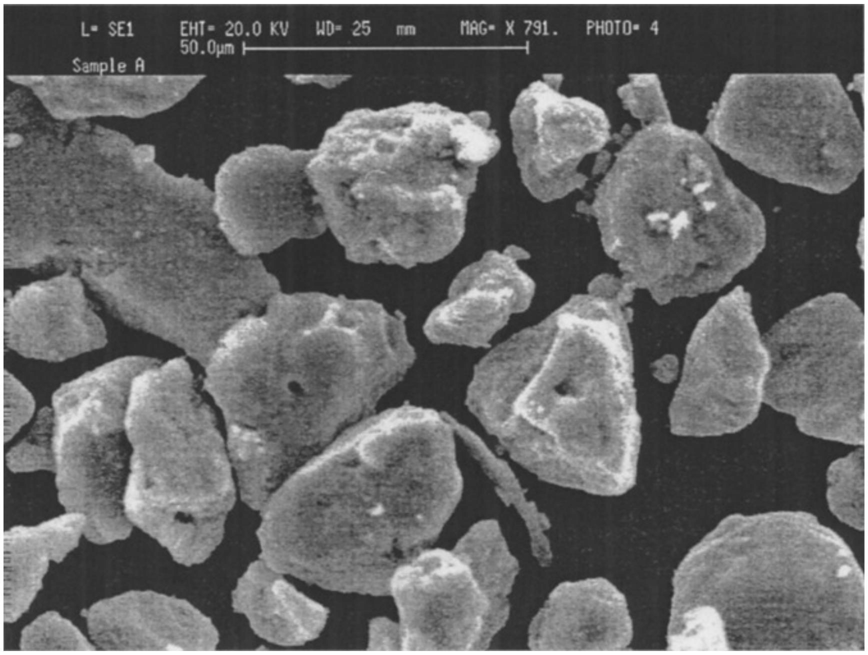


Figure 1. Scanning electron micrographs of tianina prepared in our laboratory.

certain conditions, e.g, when di-, tri- or hydoxylcarboxylic acids are used as the eluents or for the test solutes.

The changeover from one mode of exchange to another is gradual and occurs in the vicinity of the isoelectric point (pI = 5.0). This suggests that under appropriate condition of buffer and pH, titania is both a monofunctional and polyfunctional ion exchanger (16). Hence, in subsequent studies, the effect of eluent pH, the type of buffer and its concentration on the retention of anions and cations was examined.

Retention Behaviour of Anions Using Carboxylic Acidic Eluents

As mentioned previously, anion-exchange behaviour for titania column becomes more pronounced at low pH (pI = 5.0). In this study, mono-, di- and tri-carboxylic acids were used as acidic eluents to examine the effect of eluent pH and the types on the retention of anion. In addition, non-coordinating anion [29] such as NO_3^- and Cl^- were used as target solutes, as there is no ligand exchange effect at the surface of Titania.

The retention of NO_3^- on the titania column was investigated using various carboxylic acidic eluent with different concentration as shown in Figure 2. Obviously, the retention of NO_3^- strongly depends on the type of eluent, where the retention order is: acetic (11 min) > formic (9 min) > boric = water (2.2 min) > oxalic = citric acid (1.2 min). This suggests that anion and ligand exchange does occur on the titania column using various eluents as predicted in eqns (1–3). The anion-exchange behaviour becomes more pronounced at low pH values. The retention times of NO_3^- using acetic and formic acidic eluent are longer than those obtained using boric and water eluents.

In contrast, NO_3^- is not retained on the titania column using oxalic acid and citric acid as eluents even under acidic conditions. In this case, the retention mechanism on the titania column is dominated by ligand exchange between the oxalic or citric acid and titanium, and hence lead to a unretained of NO_3^-. Formation of a chelate ring between two oxygen atoms of the carboxylate anion and titanium occurs and hinder the anion-exchange between NO_3^- and titanium. This is supported by investigations on the retention behaviour of hydroxy and other substituent aliphatic carboxylic acids on titania and zirconia (25), where ligand exchange between metal ions and two oxygen atoms of the hydroxyl group and carboxylate anion results in the formation of chelate ring.

Furthermore, the retention of NO_3^- decreases as the concentration of the acetic or formic acid in the eluent is increased. As more acetate or formate anions are present in the eluent, they compete for the anion exchange site with NO_3^-. This leads to a reduction in the retention of NO_3^- (16). It is interesting to note that when the eluent pH is above the isoelectric point (pI = 5.0), the

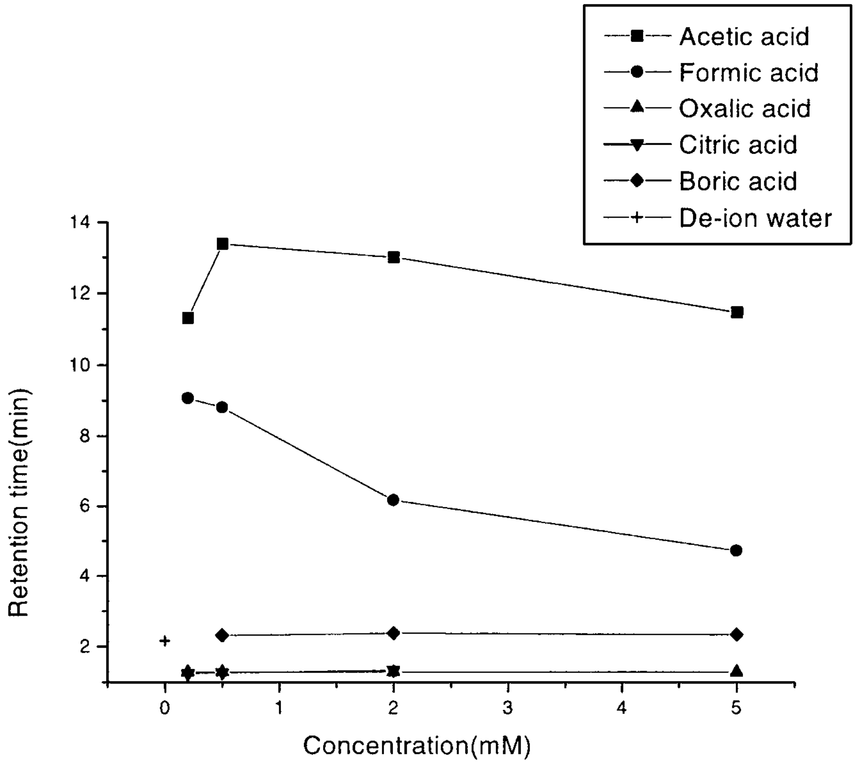


Figure 2. Effect of eluents concentration on retention time of NO_3^-.

NO_3^- retention remains constant using water (pH = 5.6) or boric acidic (pH = 5.9) eluent. This indicates that the competing anions do not significantly compete with the anion sites on the titania column. Similarly, since a strong ligand-exchange occurres between di- or tric carboxylic acid and titaina, NO_3^- would not be retained.

Figure 3 shows that the retention of NO_3^- increases as the eluent pH is decreased to near or below the pI (pH = 4.0–6.0). This indicates that a pH below the isoelectric point is required to generate anion-exchange sites as described in eqns (1–2). Moreover, a longer retention of NO_3^- using acetic acid eluent than that obtained using formic acid was observed over the tested pH range. This suggests that competing anions influence retention due to mass action and affinity of the competing anion for the titania anion-exchange site (30). In this case, the affinity of formate for anion-exchange sites is stronger than that of acetate, leading to a shorter retention of NO_3^- using formic acid as an eluent.

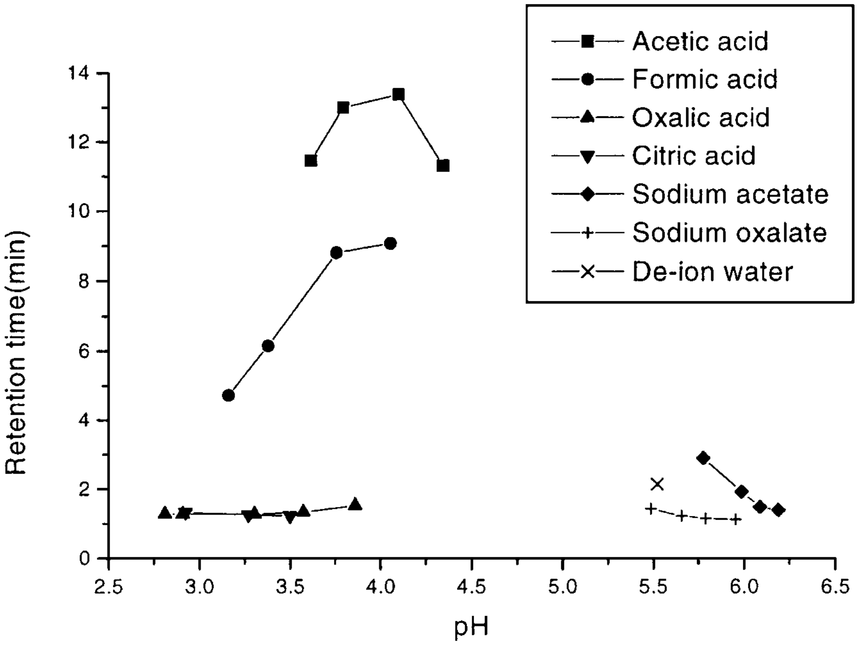


Figure 3. Relationship between eluents pH with NO_3^- retention time.

In order to examine the effect of eluent pH on the retention of NO_3^-, sodium acetate was used as the eluent. As shown in Figure 2, retention of NO_3^- is reduced significantly with sodium acetate. High pH values (>5.75) cause a reduction in the anion-exchange sites on the surface of titania as predicated in eqns (1) and (2).

Retention of Cations with Carboxylic Acidic Eluents

From eqns (1) and (2), cation exchange behaviour would be expected to appear at or above the isoelectric point ($pI = 5$). The retention of cations, including Li^+, Na^+, K^+ and $NH_4{}^+$, was investigated using various carboxylic acids due to their pH ranged between 4–6. Figure 4 shows the retention of K^+ on the titania packing column using various carboxylic acidic eluents. It can be seen that the retention of K^+ depends on the type of the eluent, and their eluent pH. The retention order is sodium acetate (10.5 min, pH: 5.5) > oxalic acid (3.8 min, pH; 1.50) > citric acid (2.8 min, pH: 3.1) > acetic (1.5 min, pH: 4.8) > formic acid (1.4 min, pH: 3.7). The eluted order of K^+ on the cation exchange mode is in contrast to that of NO_3^- on the anion and ligand exchange modes.

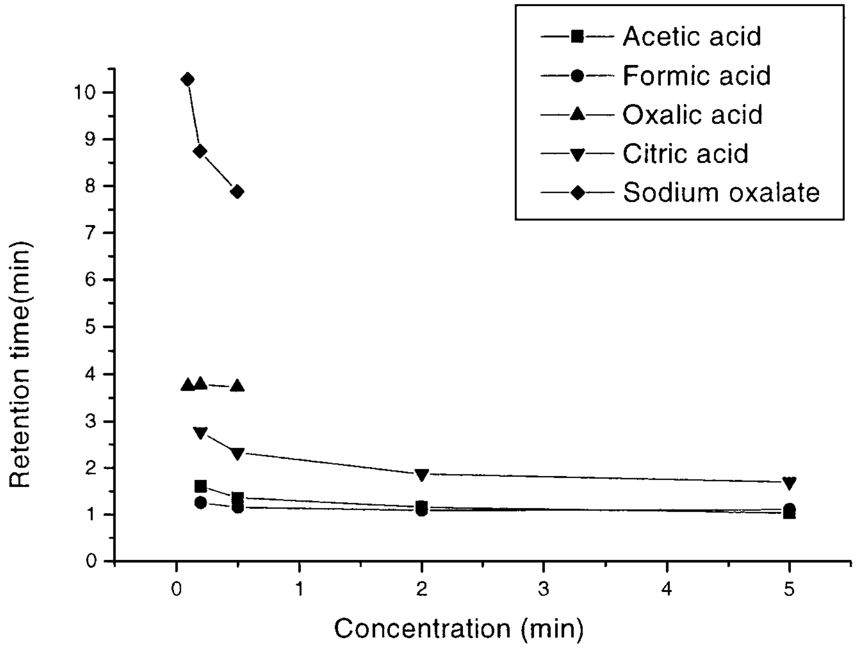


Figure 4. Effect of eluents concentration on retention time of K^+.

These results show that pH has a complex effect on cation retention because retention is influenced simultaneously by the type of the eluent and its pH. In generally, the retention of K^+ increased with decreasing eluent pH, e.g, the longest retention of K^+ was obtained using a sodium acetate eluent, while the shortest retention was achieved using a formic acidic eluent. Exceptions were oxalic and citric acid eluents, for which the retention of K^+ increased as the eluent pH decreased. This may be attributed to ligand exchange between titanium and two oxygen atoms of carboxylate anion and the formation of chelate ring as mentioned in the previous section.

As shown in eqn (3), the COO^- group touches the surface by the interaction, resulting in K^+ retaining on the titaina packed column (16). In the cases of di- and tri carboxylic eluents, the titania column exhibits both anion and ligand exchange behaviour. In addition, the decrease in retention of K^+ with increasing concentration of carboxylic acid eluent resulted in the competition of cations such as H^+ and Na^+ for the cation sites on the surface of titania, and lead to a reduction in the retention of K^+.

The retention of a number of cations was further examined using oxalic acid and sodium oxalate as the eluent. As shown in Figure 5, retention for the test cations

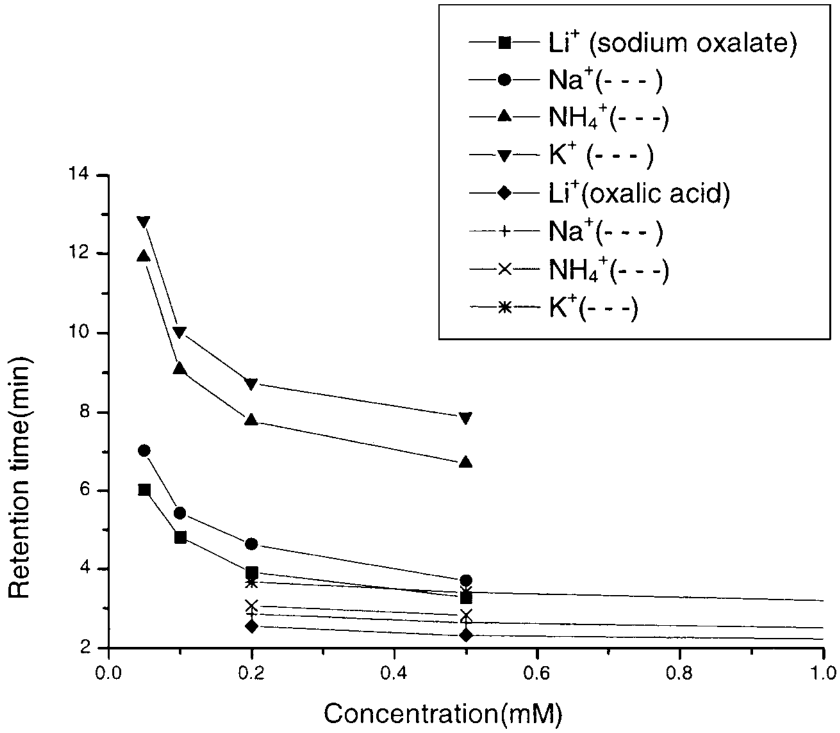
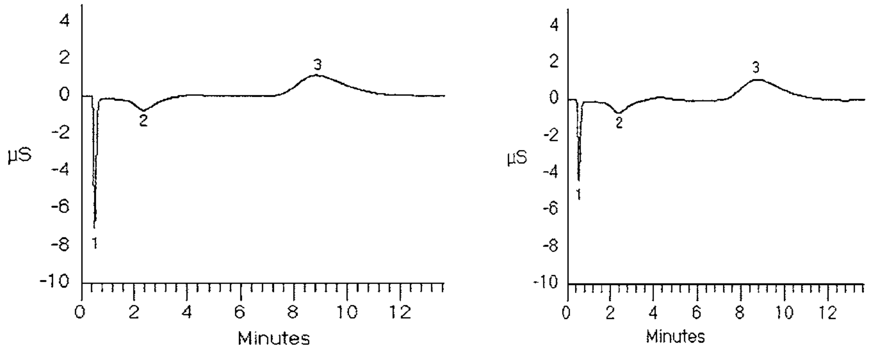


Figure 5. Retention of cations using oxalic acid and its sodium salt as eluents.

using sodium oxalate was longer than that using oxalic acid. As predicated by eqn (3), the $^{-}$OOC–COO^{-} group in the sodium oxalate eluent interacts with titanium for stronger than that of HCOO–COOH in the oxalic eluent because the former was totally ionised. Consequently, the $^{-}$OOC–COO^{-} group, with two negative charges, acted like an anion-exchanger, leading to a higher affinity for the cations and hence longer retention of the test cation (30). The order of retention for the test cations: $K^+ > NH_4{}^+ > Na^+$, $>Li^+$, which could be correlated with the diameters of the hydrated ions (31).

Separation of Anion and Cation and Ligand Effect

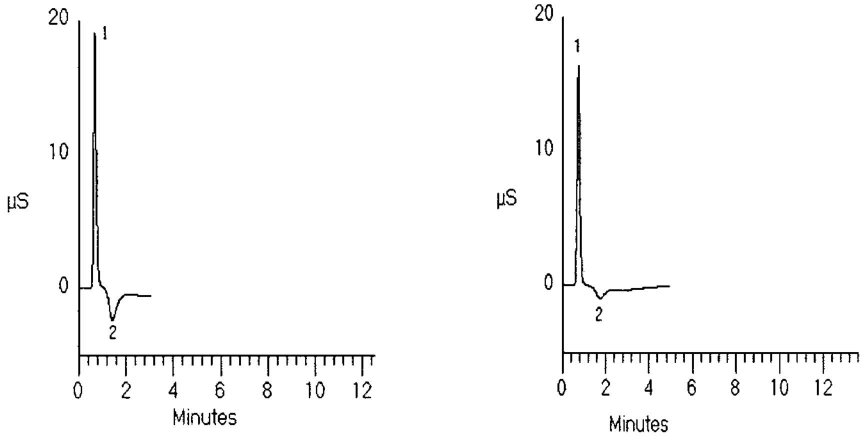
On the basis of the above results, titania packing columns demonstrated both ion and ligand exchange properties when using various carboxylic acid eluents. The changeover from one mode of exchange to the other was gradual and occurred in



A B

Figure 6. Chromatograms of 2 mM acetic acid eluent. A, Peak 1: Na^+, Peak 2 H_2O, Peak 3: Cl^-. B, Peak 1: K^+; Peak 2 H_2O , Peak 3: NO_3^-.

the vicinity of the isoelectric point. Simultaneous separation of anions and cations may be possible if an appropriate eluent could be employed. Such simultaneous separation of anions and cations using carboxylic eluents is shown in Figures 6(a) and (b), as well as 7 (a) and (b). Figures 6 (a) and (b) represents the separation of Na^+, Cl^-, and K^+, NO_3^- using acetic acid eluents.



A B

Figure 7. Chromatograms of 0.5 mM oxalic acid eluent. A. Peak 1: Cl^-, Peak 2: Na^+. Peak 1: NO_3^-, Peak 2: K^+.

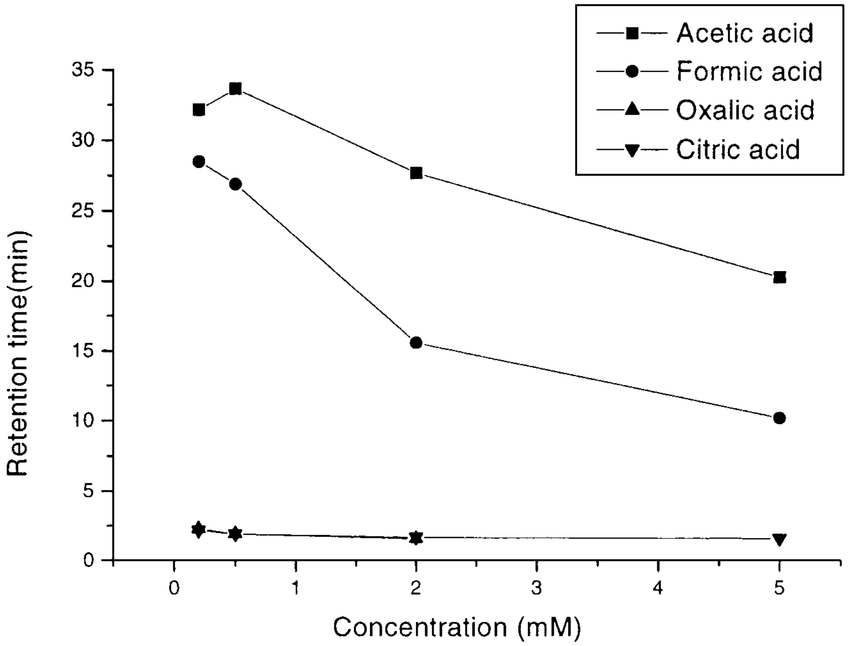


Figure 8. Effect of carboxylic acid eluents on retention of benzoic acid.

Figures 7(a) and (b) are the chromatograms of Na^+, Cl^-, and K^+, NO_3^- using an oxalic acid eluent. The eluted order for the test ions was reversed using acetic acid when compared to an oxalic acid eluent. This may result from occurring ion-exchange using acetic acid eluent, while oxalic acid used as an eluent demonstrates both ligand and ion exchange characteristics.

In order to examine the ligand exchange effect on the titania packing columns, benzoic and salicylic acids were selected as target solutes due to their strong Lewis base property and hence have a strong interaction with titania by chelation (16, 17) as shown in Figure 8. The order of retention of bezonic acid using 0.5 mM carboxylic acid eluent is acetic (32.5 min) > formic (27 min) > oxalic = citric acid (2.5 min). Clearly, a longer retention was obtained using acetic or formic eluents since acetic or formic did not interact with titanium by chelation, while benzoic acid coordinated with titanium and hence was strongly retained on the column. As a consequence, a longer retention time was obtained.

Furthermore, the retention time decreased as the concentration of acetic or formic acid increased. This resulted from competition with anions such as CH_3COO^- or $HCOO^-$ for exchange sites, e.g, the competing anion increased with increasing eluent concentration, leading to a reduction in the retention time.

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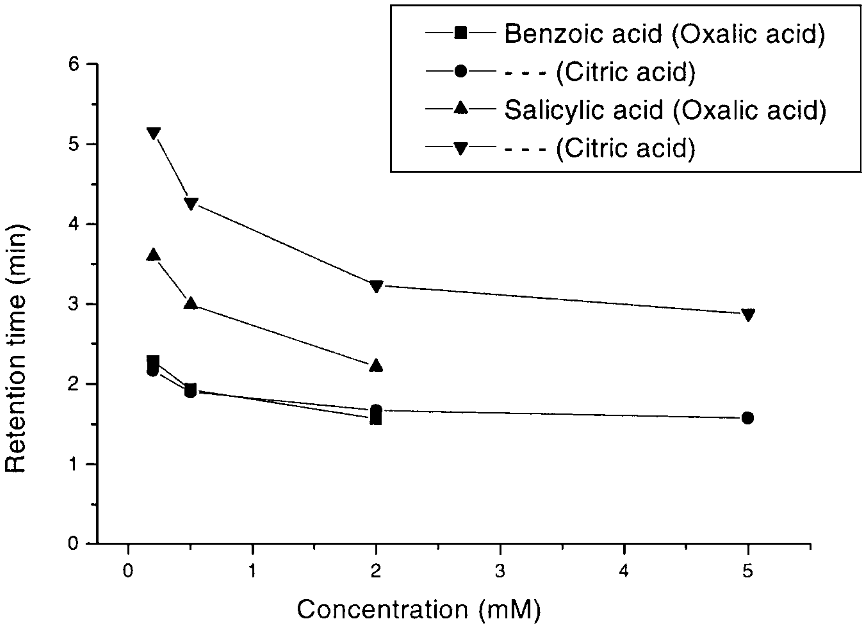

Figure 9. Retention of benzoic acid and silycylic acid under polycarboxylic acids.

In contrast, benzoic acid was unretained on the titania column because the oxalic or citric acid strongly interacted with Ti by the formation of a chelate ring, and therefore excluded the interaction of benzonic acid with titania (25). This was supported by a subsequent study shown in Figure 9, where the retention of salicylic acid was compared to that of benzoic acid using oxalic or citric eluents.

It can be seen that salicylic acid was retained on the column at lower concentrations of oxalic or citric eluent. Salicylic acid has hydroxyl and carboxyl groups and can easily form a five-member ring between titanium and two oxygen atoms of hydroxyl and carboxyl group than that of oxalic or citric acid, and it therefore retained on the titania column. Similar results were also observed by Tani et al. (25).

CONCLUSION

The results presented here have shown that titania packed columns exhibit both ion and ligand exchange characteristics, which depend largely on the eluent pH and the type of eluent. The separation of anions, cations and benzonic carboxylic acids were possible by selection of the appropriate carboxylic acid eluents.

Simultaneous separation of anion and cation was demonstrated using acetic or oxalic eluents. Further work will be concerned with the modified titania material to improve the separation selectivity and allow a number of anions and cations to be separated.

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REFERENCES

1. Helander, W.R.; Horvath, C. *High Performance Liquid Chromatography-Advances and Perespectives*; Horvath, C., Ed; Academic Press: New York, 1980; Vol 2, 113–319.
2. Willison, M.J.; Clark, A.G. Anal. Chem. **1984**, *56*, 2992.
3. Jenke, D.R.; Pagenkopf, G.K. Anal. Chem. **1983**, *55*, 1168.
4. Pietrzyk, D.J.; Chu, C.H. Anal. Chem. **1977**, *49*, 754.
5. Siomth, R.M. J. Chromatogr. **1984**, *291*, 372.
6. Dawkins, J.W.; Lopd, L.L.; Warner, E.P. J. Chroamtogr. **1986**, *352*, 157.
7. Hanai, T.; Aria, Y.; Hirukawa, M.; Noguchi, K.; Yanaghara, Y. J. Chromatogr. **1985**, *349*, 323.
8. Benson, J.R.; Woo, D.J. J. Chromatogr. Sci. **1984**, *22*, 386.
9. Schmitt, C.L.; Pietrzyk, D.L. Anal. Chem. **1985**, *57*, 610.
10. Laurent, C.L.; Billiet, H.A.; deGalan, L. Chromatographia **1983**, *17*, 253.
11. Lederer, M.; Polcaro, C. J. Chromatogr. **1973**, *84*, 379.
12. Rigney, M.P.; Weber, T.P.; Carr, P.W. J. Chromatogr. **1989**, *484*, 273.
13. Trudinger, U.; Muller, G.; Unger, K.K. J. Chromatogr. **1990**, *535*, 111.
14. Chicz, R.M.; Shi, Z.; Regnier, F.E. J. Chromatogr. **1986**, *359*, 121.
15. Kawachara, M.; Hakamura, H.; Nakajima, T. Anal. Sci. **1989**, *5*, 763.
16. Clearfield, C.L. *Inorganic Ion Exchange Materials*; CRC Press: Boca Raton, FL, 1982.
17. Laurent, C.L.; Billiet, H.A.; deGalan, L. Chroamtographia **1983**, *17*, 394.
18. Laurent, C.L.; Billiet, H.A.; deGalan, L. J. Chromatogr. **1984**, *285*, 161.
19. Mcneff, J.A.; Carr, P.W. Anal. Chem. **1992**, *67*, 3886.
20. Hu, J.; Carr, P.W. Anal. Chem. **1992**, *70*, 1934.
21. Wirth, H.J.; Erikkson, K.O.; Holt, P.; Aguilar, M.; Hearn, M.T.W. J. Chromatogr. **1993**, *646*, 129.
22. Tani, K.; Suzuki, Y. J. Chromatogr. A. **1996**, *722*, 129.
23. Tani, K.; Suzuki, Y. Chromatographia **1997**, *46*, 623.

24. Tani, K.; Kubojima, H. Chromatographia **1998**, *47*, 655.
25. Tani, K.; Ozawa. M. J. Liq. Chrom. & Rel. Technol. **1999**, *22*, 843.
26. Pesk, J.J.; Matyska, M.T.; Ramakrishnan, J. Chromatographia **1997**, *44*, 538.
27. Ellwanger, A.; Matyska, M.T.; Albert, K.; Pesk, J.J. Chromatographia **1999**, *49*, 424.
28. Kurganov, K.; Trudinger, U.; Isaeva, T.; Unger, K. Chromatographia **1996**, *42*, 217.
29. Nawrocki, J.; Rigney, M.P.; McCormick, A.; Carr, P.W. J. Chromatogr. A. **1993**, *657*, 229.
30. Weiss, J.; *Ion Chromatography*, 2nd Ed.; VCH: Weinheim, New York, 1995.
31. Stahlberg, J. J. Chromatogr. **1986**, *356*, 231.

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