



ELSEVIER

Journal of Chromatography A, 964 (2002) 113–122

JOURNAL OF
CHROMATOGRAPHY A

www.elsevier.com/locate/chroma

Retention of alkali, alkaline earth and transition metals on an itaconic acid cation-exchange column

Eluent pH, ionic strength and temperature effects upon selectivity

Wasim Bashir, Eadaoin Tyrrell, Orlagh Feeney, Brett Paull*

National Centre for Sensor Research, School of Chemical Sciences, Dublin City University, Dublin 9, Ireland

Received 25 February 2002; received in revised form 26 April 2002; accepted 19 May 2002

Abstract

The unusual selectivity of a methylene succinic (itaconic) acid modified polymeric column was investigated for the separation of alkali, alkaline earth, transition and heavy metals employing non-chelating inorganic eluents. The retention of selected metal ions on the column was investigated with simple HNO_3 eluents and eluents prepared from KNO_3 and KCl salts of varying pH (adjusted using HNO_3). From these studies both the effect of eluent ionic strength and pH upon retention was evaluated for the itaconic acid stationary phase. The results obtained showed that despite slow exchange kinetics causing poor efficiencies, acceptable baseline separations of selected alkaline earth and transitions could be obtained under optimum conditions (the baseline separation of Mg(II) , Ca(II) , Mn(II) , Cd(II) , Zn(II) and Co(II) was possible using a 15 mM KNO_3 –5 mM KCl eluent at pH 3.50 in under 25 min). The use of a simple ionic strength step gradient was shown that facilitated the addition of Pb(II) to the above group of metal ions. An investigation into the effect of temperature upon peak efficiency and retention showed increased column temperature could be used to improve the resolution of closely eluting metal ions such as Ca(II) and Sr(II) and Ca(II) and Mn(II) . © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Stationary phases, LC; pH effects; Temperature effects; Ionic strength; Selectivity; Itaconic acid; Metal cations; Alkali metals; Alkaline earth metals; Transition metals

1. Introduction

The use of ion chromatography for the determination of alkali, alkaline earth and transition metal ions in water samples presents a useful alternative to atomic spectroscopic techniques and as such is often the method of choice in many analytical laboratories. With this in mind it is not surprising that a great deal of research effort has focused on the development of

new stationary phases that can offer useful selectivities for these and other less common metal ions. Most of these recent developments in stationary phase technology for the separation and determination of metal ions using various modes of ion chromatography are detailed in recent review articles by Sarzanini and Mentasti [1] and Pohl and colleagues [2,3].

In its early stages ion chromatography was very much seen as purely being based upon the use of simple ion-exchangers as the stationary phase. For cations these were primarily either carboxylated or sulphonated resins or silica gels. However, the

*Corresponding author. Tel.: +353-1-700-5060; fax: +353-1-700-5503.

E-mail address: brett.paull@dcu.ie (B. Paull).

selectivity exhibited by these cation-exchange phases was limited and so new phases with more than one type of ion-exchange group were developed, such as carboxylic/phosphonic acid functionalised columns (Ionpac CS12A), which showed improved selectivity for the simultaneous isocratic separation of alkali and alkaline earth metal ions.

More recently however, it has become clear that even greater selectivity, can be obtained through the inclusion of alternative retention mechanisms or solute interactions within the system, in particular stationary phase complexation or chelation has received much attention. For example, Ionpac CS15 contains crown ethers in addition to carboxylic/phosphonic acid groups, which acts to alter the selectivity of the column for those cations that can be complexed by the ligand. Alternative functional groups have also been investigated which possess the ability to retain the metal ion through both a simple ion-exchange mechanism and also through chelation/complexation. The extent to which either of these two retention mechanisms occurs is dependent upon eluent conditions such as pH, ionic strength and temperature. Examples of functional groups which have this chelation/ion-exchange capability are iminodiacetic acid (IDA), aminophosphonic acid and glutamic acid, all of which have been investigated regarding their application to the separation of alkali, alkaline earth and transition metal ions in earlier studies [4–8]. In each case unusual selectivities could be obtained due to what could be described as a dual retention mechanism. The use of such complexing stationary phases for the separation of metal ions in ion chromatography is the subject of a review by Jones and Nesterenko [9].

In this current study a methylene succinic acid (itaconic acid) functionalised polymeric stationary phase was evaluated for its selectivity for alkali, alkaline earth and common transition metal ions. To the authors' knowledge there has been no published studies into the selectivity of an itaconic acid resin for the above range of metal ions and so this selectivity was investigated here. As itaconic acid contains two carboxylate groups potential exists for complexation to play a role in retention, namely coordination of the metal ion with two oxygen donor atoms. The high degree of selectivity shown by the resin for certain transition metals over alkaline

earth metals certainly indicates this to be the case. However, as shown in this study, eluent pH, ionic strength and manipulation of column temperature, can be used to control the degree of each retention mechanism occurring and thus achieve several useful separations of metal ions from each of the above groups.

2. Experimental

2.1. Instrumentation

A Dionex model GPM2 gradient pump module (Sunnyvale, CA, USA) was used to deliver the eluent (1.5 ml/min). A manual sample injection valve, model 7125 (Rheodyne, Cotati, CA, USA), fitted with a 250- μ l injection loop was used for introduction of the samples. The analytical column was a 150 \times 4.0 mm I.D. PRP-X800 cation-exchange column (particle size 7 μ m) supplied by the Hamilton Company (Reno, NV, USA). A pressure-driven Dionex reagent delivery module was used for introduction of the postcolumn reagent (1.5 ml/min), which was mixed with the eluent postcolumn using a 0.5-m polyether ether ketone (PEEK) reaction coil (0.01 in. I.D; 1 in.=2.54 cm). A model SPD-6AV Shimadzu UV-vis detector (Kyoto, Japan) was used to monitor the resultant chromatograms at 510 or 570 nm (see below). These were recorded using Dionex AI450 chromatographic software. For the work on the effect of eluent temperature upon the retention of alkali metal ions a Dionex DX120 ion chromatograph was used employing indirect conductivity detection.

2.2. Reagents

The eluent and postcolumn reagent (PCR) were prepared using deionised water from a Millipore Milli-Q water purification system (Bedford, MA, USA). The postcolumn reagents used, 4-(2-pyridylazo) resorcinol (PAR) and *o*-cresolphthalein complexone (*o*-CPC), and sodium hydroxide were purchased from Sigma-Aldrich (Gillingham, UK) and used without further purification. Potassium nitrate was obtained from Merck (Darmstadt, Germany) and potassium chloride from Fluka (Buchs,

Switzerland). For the detection of transition metal ions the postcolumn reagent solution was 0.5 M ammonia, 0.4 mM PAR, adjusted to pH 10.5 (monitored at 510 nm). For the detection of alkaline earth metals this was 0.4 mM *o*-CPC, 0.25 M boric acid adjusted to pH 10.5 using NaOH (monitored at 570 nm). All standard solutions prepared were filtered through a 0.45- μ m filter and degassed using sonication. Low level standard solutions were generally prepared freshly each day from stock solutions (1000 mg/l) stored in 1% nitric acid.

3. Results and discussion

3.1. Inorganic eluents

In this work the retention behaviour of alkali, alkaline earth and common transition and heavy metal ions on the itaconic acid stationary phase was evaluated using simple inorganic eluents. Initially, three eluents were investigated—HNO₃, KNO₃ and KCl. As itaconic acid contains two weak carboxylic acid groups ($pK_{a1}=3.85$, $pK_{a2}=5.45$ [10]), eluent pH will have a large affect upon metal ion retention due to the strong affinity of H⁺ for the carboxylate groups. With simple dilute HNO₃ eluents the itaconic acid stationary phase exhibited similar selectivity to other dicarboxylate stationary phases, such as IDA [6,8]. With HNO₃ eluents the stationary phase selectivity was determined as follows; Li<Na<NH₄<K<Cs<Mg(II)<Ca(II)≤Sr(II)<Mn(II)≤Ba(II)<Cd(II)<Zn(II)<Co(II)≪Pb(II)≪Cu(II). For the alkali and alkaline earth metal ions the retention order shown was close to that expected if only ion-exchange were responsible for retention, as would be the case on a sulphonated cation-exchanger. However, for the transition and heavy metals investigated the selectivity was close to the reverse of that expected if only ion-exchange were taking place. In particular, the itaconic acid stationary phase showed strong selectivity towards Pb(II) and Cu(II) ions over the remainder of the above metals, with strongly acidic eluents (up to 50 mM HNO₃) being required for their elution from the column. Under such acidic conditions all the other metal ions tested were unretained, such that it was possible to selectively separate and determine Cu(II)

in samples containing a mixture of all of the above metal ions. Fig. 1a shows the strong affect of pH (HNO₃ eluent) upon retention of the alkaline earth and transition metal ions using the itaconic acid column. The retention slopes obtained for each of the metals injected were all very similar, ranging from −1.802 for Mn(II) to −1.978 for Cu(II). Fig. 1b demonstrates the unusual selectivity for Cu(II) with overlaid chromatograms of Ca(II), Pb(II) and Cu(II) standards, obtained using a 30 mM HNO₃ eluent. As can be seen from Fig. 1b it was evident that peak shapes rapidly became broad with relatively small increases in retention. This effect is often seen in chromatographic systems where more than one retention mechanism is taking place and is a strong indication of stationary phase chelation occurring, as complex formation/dissociation kinetics are general-

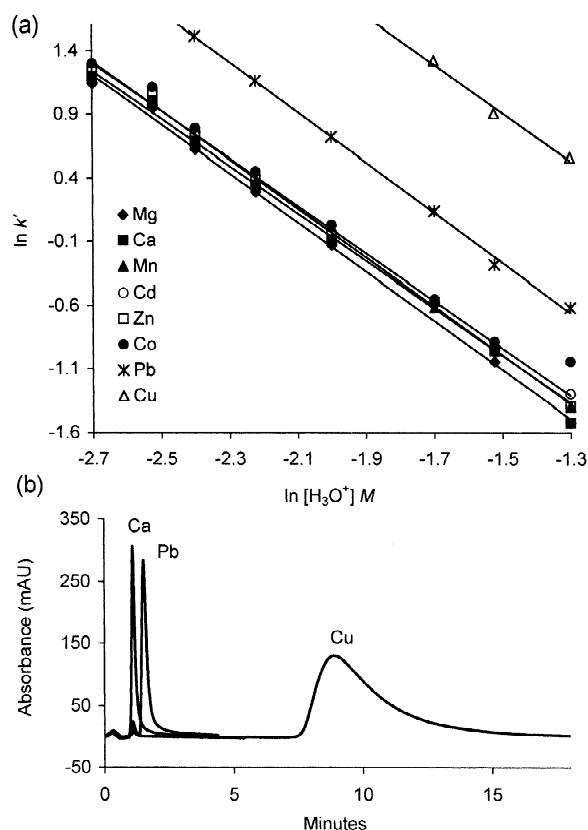


Fig. 1. (a) Effect of eluent pH on capacity factors (k') of alkaline earth and transition metals. (b) Overlaid chromatograms of Ca(II) (5 mg/l), Pb(II) (2 mg/l) and Cu(II) (2 mg/l) standards obtained using a 30 mM HNO₃ eluent. Detection using PCR with PAR.

ly much slower than the kinetics of simple ion-exchange [9]. The peak broadening shown was independent of standard concentration, with lower concentration standards being equally broad, this then eliminating column overload as a possible cause of the rather poor peak shape. In comparison with our previous work using dicarboxylate chelating ligands, namely IDA bonded 8- μm silica gels [6–8], it can be qualitatively stated that the efficiency of the itaconic acid resin was clearly poorer, this being an obvious disadvantage of the new polymer phase.

Where stationary phase complexation/chelation is contributing to retention it is expected that the effect of eluent ionic strength upon retention will be less than that seen if simple cation-exchange were the only retention mechanism. Therefore, the effect of eluent ionic strength upon retention was investigated here using varying ionic strength eluents prepared from nitrate and chloride potassium salts. The pH of all the eluents investigated was kept constant and slightly acidic at pH 3.3 to minimise error and ensure capacity factors were under 20 for the weakest eluents used. The effect of ionic strength was investigated over the range 0.02–1.0 M KNO_3 and KCl. The resultant log retention graphs are shown as Fig. 2a and b, respectively. As expected the selectivity of itaconic acid for K^+ is much lower than for H^+ . Slopes obtained for the KNO_3 eluent ranged from -0.607 for $\text{Mg}(\text{II})$ to -0.948 for $\text{Zn}(\text{II})$. The eluents prepared using KCl proved to be the stronger eluents due to the added weak complexing ability of the chloride ions, here slopes ranged from -0.969 for $\text{Mg}(\text{II})$ to -1.346 for $\text{Co}(\text{II})$. Under all the eluent conditions tested $\text{Cu}(\text{II})$ was fully retained, even with the 1 M KCl eluent. The retention of $\text{Pb}(\text{II})$ was also considerable with retention times of >50 min when using a 0.1 M KCl eluent. Even with a 0.5 M KCl eluent (at pH 3.3) $\text{Pb}(\text{II})$ was retained for 8 min, illustrating the unusually selective properties of the itaconic acid functional group.

3.2. Metal separations

Using only dilute HNO_3 (0.6–2 mM) eluents separations of $\text{Mg}(\text{II})$, $\text{Ca}(\text{II})$, $\text{Mn}(\text{II})$, $\text{Cd}(\text{II})$, $\text{Zn}(\text{II})$ and $\text{Co}(\text{II})$ could be obtained using the itaconic acid column, with $\text{Pb}(\text{II})$ and $\text{Cu}(\text{II})$ totally retained. However, under these conditions run times were

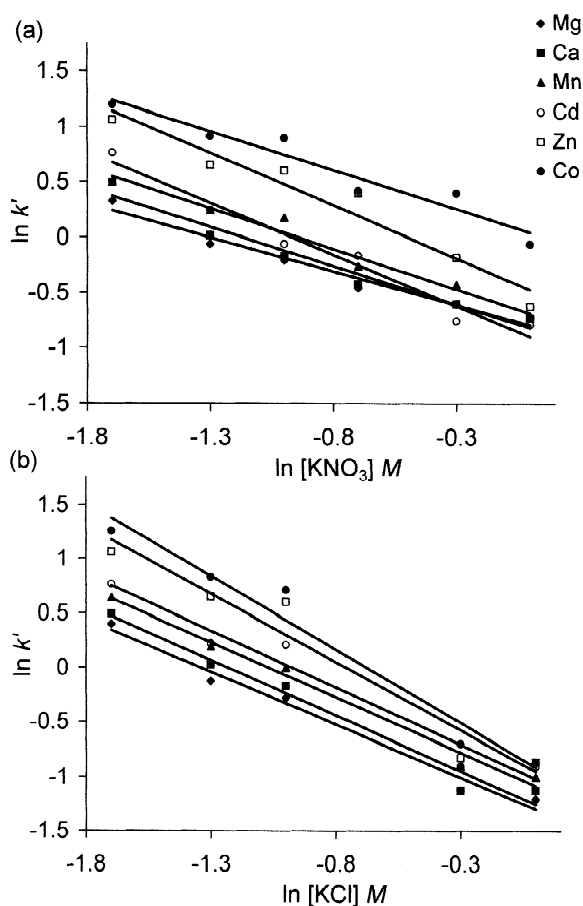


Fig. 2. Effect of eluent ionic strength on retention using a (a) KNO_3 eluent and (b) KCl eluent (pH adjusted to 3.3 using dilute HNO_3). Standard concentration 2 mg/l.

excessive (up to 30 min), as peak shapes were rather poor, particularly for the later eluting metal ions. More acidic eluents resulted in co-elution of the early eluting peaks of $\text{Mg}(\text{II})$, $\text{Ca}(\text{II})$ and $\text{Mn}(\text{II})$. Addition of either KNO_3 or KCl (20 mM) to the above eluents was investigated to see if peak shapes improved. As expected this led to a reduction in retention times and a slight improvement in peak shapes. In both cases the resolution of $\text{Mn}(\text{II})$ from the early eluting peaks of $\text{Mg}(\text{II})$ and $\text{Ca}(\text{II})$ was improved. However, the additions also caused the co-elution of $\text{Cd}(\text{II})$ and $\text{Zn}(\text{II})$ with the KNO_3 eluent and $\text{Zn}(\text{II})$ and $\text{Co}(\text{II})$ with the KCl eluent. Typical chromatograms obtained using the above eluents are shown in Fig. 3a–c. To facilitate the

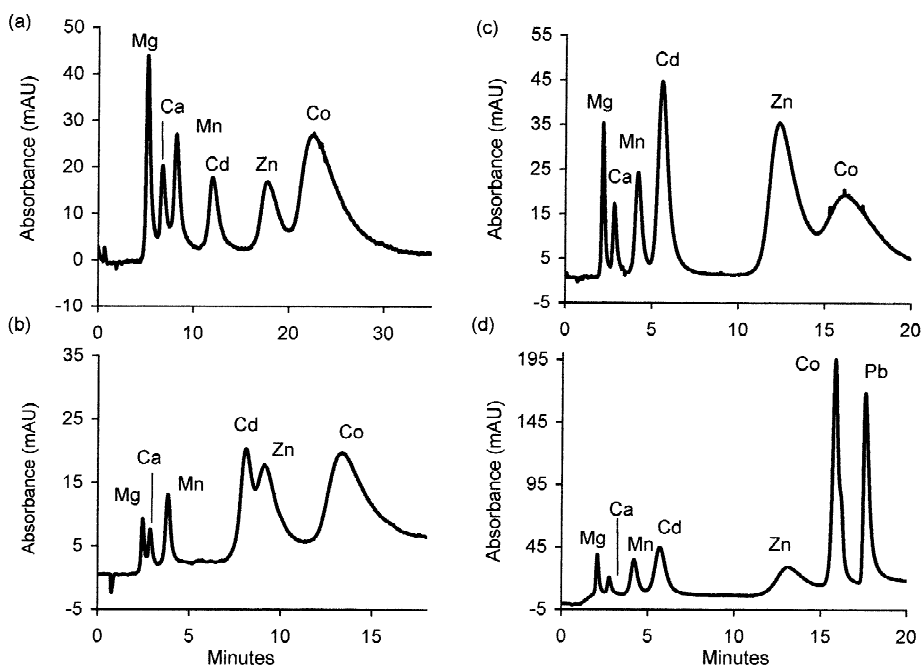


Fig. 3. Chromatograms showing the separation of Mg(II), Ca(II), Mn(II), Cd(II), Co(II) and Zn(II) using (a) a HNO_3 eluent (pH 2.7), (b) a 20 mM KNO_3 eluent (pH 3.3), (c) a 20 mM KCl eluent (pH 3.3) and (d) a 20 mM KCl eluent (pH 3.4) increased to 1 M KCl (pH 3.4) between 11 and 12 min. Detection using PCR with PAR. Standard concentrations between 0.5 and 5 mg/l.

elution of Pb(II) and Cu(II) from the column, both pH and ionic strength gradients were investigated. However, it was found that the high buffering capacity of the column due to the itaconic acid groups made using pH gradients difficult, resulting in poor reproducibility, attributed to long column re-equilibration times following each gradient run. The use of an ionic strength gradient whilst keeping the pH uniform proved more successful in terms of reproducibility and could be used to obtain a separation of Mg(II), Ca(II), Mn(II), Cd(II), Zn(II), Co(II) and Pb(II), although even when using a final eluent strength of 1 M KCl , Cu(II) was still retained. Fig. 3d shows the chromatogram obtained using a KCl gradient.

Finally, the use of mixed eluents was investigated under isocratic conditions. In an attempt to obtain the optimum resolution of the above metal ions in as short an overall run time as possible, eluents containing varying ratios of KNO_3 to KCl were prepared, keeping the total eluent concentration constant at 20 mM. The concentration of KCl had a significant effect upon the retention and resolution of the

later eluting transition metal ions, but little effect upon the retention of Mg(II), Ca(II) and Mn(II). The optimum conditions found were 15 mM KNO_3 , 5 mM KCl (pH 3.5), which resulted in the chromatogram shown in Fig. 4.

3.3. Temperature effects

The unusual selectivity exhibited by the itaconic acid column prompted an investigation into the effect of column temperature upon the retention of alkaline earth and transition metal ions. It has been shown in several previous studies that temperature can have a very different affect upon the retention of metal ions depending upon the exact mode of retention. Where only cation-exchange is responsible for retention, temperature is known to have only a small predominantly negative affect upon retention. Fortier and Fritz [11] first investigated this effect using a strong cation-exchange resin with a perchloric acid eluent. The results showed retention times of divalent metal ions decreased with an increase in system temperature. Much more recently, work by

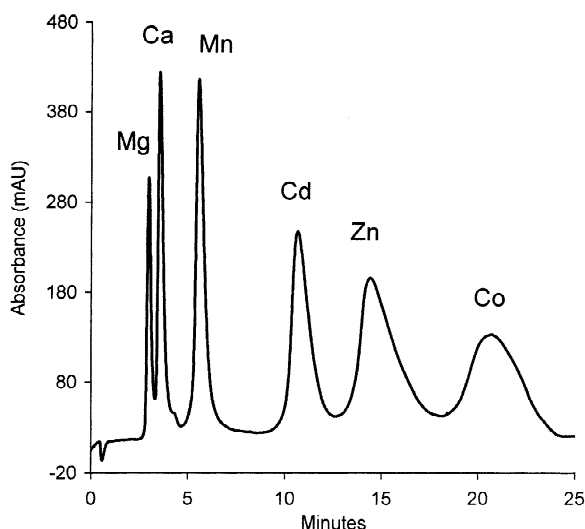


Fig. 4. Chromatogram showing the optimised separation of Mg(II), Ca(II), Mn(II), Cd(II), Zn(II) and Co(II) obtained using a mixed eluent of 15 mM KNO₃ and 5 mM KCl (pH 3.5). Standard composition: Mg(II), Ca(II), (10 mg/l) Cd(II), Co(II) (5 mg/l), Zn(II) (2 mg/l), Mn(II) (1 mg/l). Detection using PCR with PAR.

Rey and Pohl [12] and Hatsis and Lucy [13] showed similar trends when using a carboxylate/phosphonate stationary phase used with a methanesulphonic acid eluent. However, where retention of metal ions is the result of stationary phase complexation (or indeed a combination of both ion-exchange and stationary-phase complexation) the above negative effect of temperature is no longer seen. This has been illustrated recently in a number of studies on the separation of alkaline earth [6], transition metals [8] and the lanthanide metals [14] using iminodiacetic acid functionalised silica columns, where in each case under the eluent conditions studied, an increase in retention resulted from an increase in column temperature.

Fortier and Fritz [11] proposed the following equation to express the effect of column temperature upon retention ($\ln k'$) in ion-exchange;

$$\ln k' = -\frac{\Delta H^\circ}{RT} + \frac{\Delta S^\circ}{R} + \ln \phi \quad (1)$$

where ΔH° is the enthalpy of the sorption process, ΔS° is the change in entropy and ϕ is the phase ratio. Where the sorption process exhibits exothermic behaviour (negative values of ΔH°), the retention of

the analyte ion will decrease with increasing column temperature, as shown recently by Hatsis and Lucy [13]. This will present itself graphically as a positive slope in a Van't Hoff plot ($\ln k'$ vs. $1/T$). However, studies on stationary phases capable of metal ion complexation have shown much higher values of ΔH° , particularly under eluent conditions which favour stationary-phase complexation over ion exchange (high ionic strength and increased pH) [4]. Under these conditions, the sorption process exhibits endothermic behaviour, resulting in a negative slope in a Van't Hoff plot.

The plots shown in Fig. 5 depict the effect column temperature has upon retention of alkali, alkaline earth and transition metal ions using the itaconic acid stationary phase under various eluent conditions. Using simple 1- and 2-mM HNO₃ eluents, the column was first tested for retention of alkali metal ions through simple ion exchange. The results obtained were similar to those shown by Hatsis and Lucy [13] with all (bar lithium with 1 mM HNO₃ eluent) exhibiting a decrease in retention with increased column temperature when using either eluent. With the stronger 2 mM HNO₃ eluent it was possible to elute Ca(II) and Mg(II) from the itaconic acid column. With this low ionic strength eluent the effect of temperature upon retention of these alkaline earth metals was clearly different to the effect upon the alkali metals. Only a very slight decrease in retention of Mg(II) could be seen, with the retention of Ca(II) remaining unaffected by temperature.

However, as shown in Fig. 5b, when using an eluent of higher ionic strength and pH (20 mM KCl eluent adjusted to pH 3.5 using HNO₃), both Ca(II) and Mg(II) behave very differently, and now like the transition metals shown, exhibit an increase in retention with an increase in column temperature. Under these conditions it would be expected that both ion exchange and complexation would be contributing to the retention of the alkaline earth and transition metals. As complete stability constant data sets for itaconic acid complexes of alkaline earth and transition metals are not readily available, it was not possible to predict the exact contribution to retention of stationary phase complexation. However, if itaconic acid behaves similarly to other dicarboxylate ligands, it should be expected that complexation was playing a greater role in the retention of the transi-

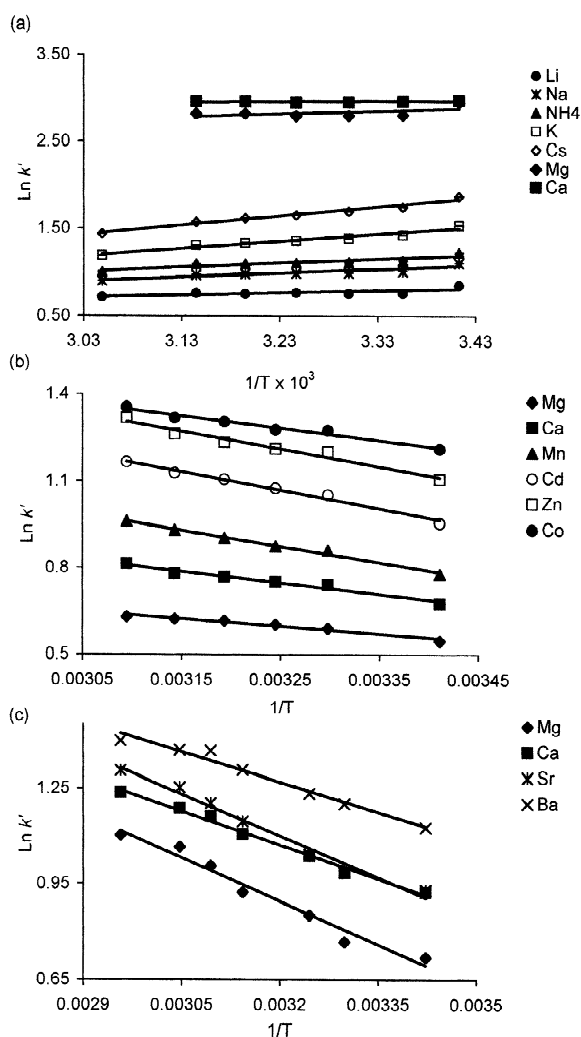


Fig. 5. Van't Hoff plots of metal retention vs column temperature. Eluent conditions: (a) 2 mM HNO_3 , (b) 20 mM KCl (pH 3.5), (c) 100 mM KCl (pH 5.7).

tion metal ions than the alkaline earth metals. The slopes obtained from the data shown in Fig. 5b (listed in Table 1) support this assumption, with temperature having significantly less effect upon the retention of the alkaline earth metals compared to the transition metals.

This nonuniform response to temperature means column temperature can be used as an extra means to manipulate selectivity. For example, under the eluent condition used in Fig. 5b, the baseline resolution of Mn(II) from Ca(II) at room temperature was not

Table 1
Slopes and correlation coefficients from Van't Hoff plots of alkali, alkaline earth and transition metals

	Slope	r^2
Eluent 1 mM HNO_3^a		
Lithium	-0.1219	0.896
Sodium	0.1012	0.843
Ammonium	0.1213	0.837
Potassium	0.5033	0.997
Cesium	0.7155	0.998
Eluent 2 mM HNO_3^b		
Magnesium	0.3356	0.319
Calcium	0.0485	0.326
Lithium	0.2517	0.596
Sodium	0.4290	0.832
Ammonium	0.4641	0.832
Potassium	0.8380	0.945
Cesium	1.0661	0.969
Eluent 20 mM KCl at pH 3.5 ^c		
Magnesium	-0.265	0.952
Calcium	-0.395	0.967
Manganese	-0.553	0.988
Cadmium	-0.637	0.984
Zinc	-0.617	0.965
Cobalt	-0.427	0.970
Eluent 100 mM KCl at pH 5.7 ^d		
Magnesium	-0.905	0.969
Calcium	-0.711	0.990
Strontium	-0.874	0.982
Barium	-0.628	0.974

^a Temperature range 20–60 °C.

^b Temperature range 20–60 °C.

^c Temperature range 20–50 °C.

^d Temperature range 19–65 °C.

possible. However, an increase in column temperature up to 50 °C caused a greater increase in the retention of Mn(II) relative to Mg(II) and Ca(II), resulting in their improved resolution (see Fig. 6).

From the above results it was predicted that if eluent conditions were such that ion-exchange interactions were minimised and complexation was the dominant retention mechanism, the effect of temperature upon the retention of alkaline earth metals would be much more pronounced. Therefore a 100-mM KCl eluent was prepared and adjusted to pH 5.7. The effect column temperature had upon the retention of alkaline earth metal ions using this eluent is shown as Fig. 5c. From the results obtained it is clear that under these conditions the effect of temperature is indeed more pronounced with consider-

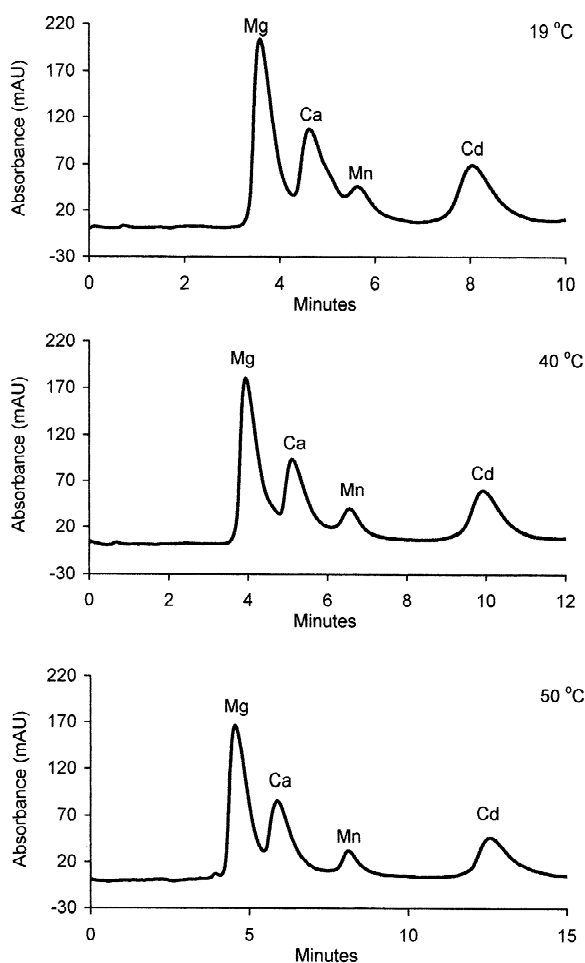


Fig. 6. Chromatograms showing the resolution of Mg(II), Ca(II), Mn(II) and Cd(II) at 19, 40 and 50 °C. Eluent conditions: 20 mM KCl (pH 3.5). Standard composition: Mg(II) (5 mg/l) Ca(II) (2 mg/l), Cd(II) (1 mg/l) and Mn(II) (0.2 mg/l). Detection using PCR with PAR.

able increases in retention for all four metals. The slopes obtained (see Table 1) are now even greater than even those obtained for the transition metal ions using the previous 20 mM KCl eluent. However, relative retention is not reflected in response to temperature, as Ba(II) being retained for the longest shows the least effect and Mg(II), which is the least retained of the four ions, shows the greatest effect. This may be a reflection upon the ion-exchange selectivity of the column. As the selectivity of most cation exchangers, including carboxylated resins, is Ba(II) > Sr(II) > Ca(II) > Mg(II), it could be that

even with the 100-mM eluent, ion exchange was playing a minor role in the retention of Ba(II) and this was being reflected in resulting slope. For Mg(II), the opposite is true, with any ion-exchange interactions likely to have been predominantly suppressed, resulting in the ion showing the greatest response to temperature. However, this hypothesis does not explain the response of Sr(II), which is almost equal to that of Mg(II). Therefore, the only absolute conclusions that can be drawn from these observations are that clearly an increase in all four alkaline earth metal ions results from an increase in column temperature and that under these eluent conditions stationary phase complexation was likely to be the dominant retention mechanism.

As before, it was clear that nonuniform responses to changes in temperature could be used to improve resolution. At room temperature, the itaconic acid column showed poor resolution of Ca(II) and Sr(II) under most eluent conditions tested. However, as can be seen from the chromatograms shown in Fig. 7, under the eluent conditions described above, temperature could be used to resolve these two metal ions, without leading to the excessive retention of Ba(II).

3.4. Sample ionic strength

Finally, the unique selectivity of the itaconic acid phase was investigated in relation to the effect of sample ionic strength. If retention was predominantly due to complexation not ion exchange, sample ionic strength should have a less detrimental effect upon the separation of the alkaline earth metals. Therefore, two alkaline earth metal mixed standards were prepared. To each standard mix Li was added as a marker for the elution of alkali metals (Li is the only alkali metal to show significant detector response when using PCR with *o*-CPC). As mentioned above the alkali metals did not show an increased retention at elevated column temperatures and were only marginally retained with the 100 mM KCl eluent. To one of the standard mixes 0.1 M NaCl was added (2.3 g/l Na). The resulting chromatograms for the two mixed standards are shown overlaid in Fig. 8. Two observations can be made from the chromatograms obtained. Firstly, the usual loss in efficiency associated with high ionic strength samples can be seen with the peak for Li, with the peak shape

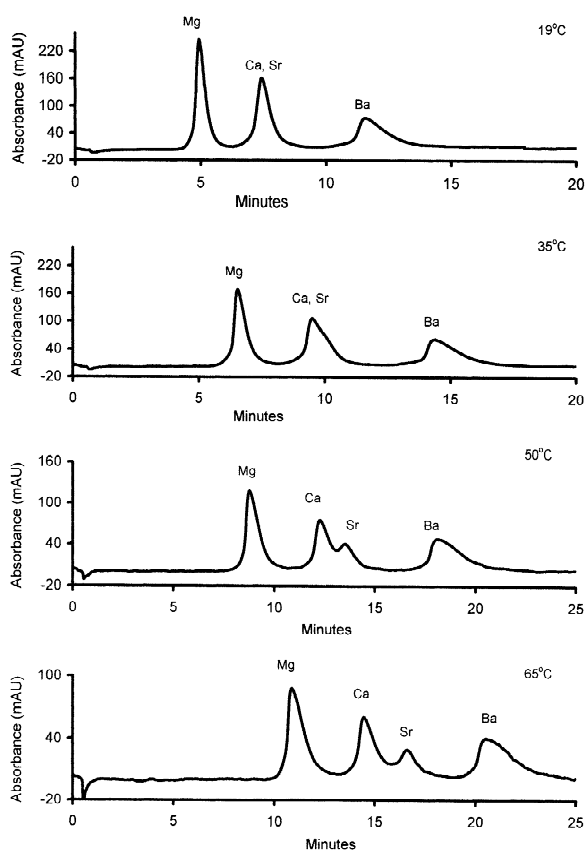


Fig. 7. Chromatograms showing the resolution of Mg(II), Ca(II), Sr(II) and Ba(II) at 19, 35, 50 and 65 °C. Eluent conditions: 100 mM KCl (pH 5.1). Standard composition: Ba (50 mg/l), Sr (10 mg/l), Mg(II) (5 mg/l) and Ca(II) (2 mg/l). Detection using PCR with *o*-CPC.

dramatically poorer. Secondly, although a slight decrease in retention can be seen for the alkaline earth metals, their overall resolution and individual peak efficiencies were unaffected. This experiment illustrates a considerable advantage of the use of such complexing stationary phases in the analysis of real samples, which are often of high ionic strength, and shows how the itaconic acid phase is suitable for the determination of alkaline earth metals in samples containing excess concentrations of alkali metals.

4. Conclusions

The results have shown the itaconic acid phase

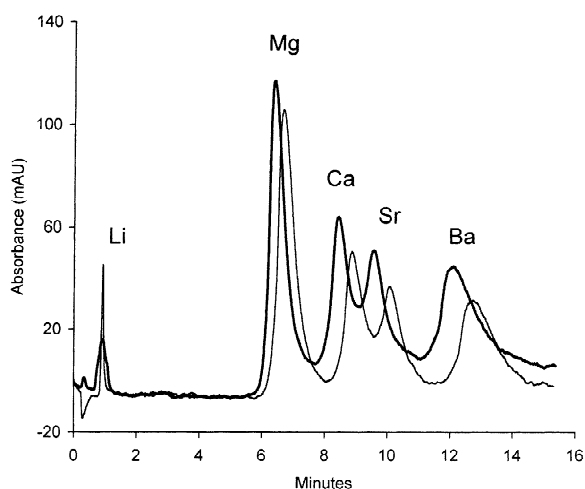


Fig. 8. Overlaid chromatograms of alkaline earth metal mixed standard solutions. Standard composition: (a) Li (70 mg/l), Ba (50 mg/l), Sr (10 mg/l), Mg(II) (4 mg/l) and Ca(II) (1 mg/l). (b) as (a) plus 2.3 g/l Na. Eluent conditions: as in Fig. 7. Column temperature: 65 °C; flow-rate: 2.5 ml/min. Detection using PCR with *o*-CPC.

exhibits unusual and useful selectivity for alkaline earth and transition/heavy metal ions resulting from a combination of both ion exchange and complexation interactions. Control of eluent pH was the most critical parameter in manipulating cation selectivity. Column temperature was shown to also affect selectivity, with an increase in column temperature causing an increase in the retention of all alkaline earth and transition/heavy metals tested, this being the opposite case to that expected if only ion exchange were taking place.

Acknowledgements

The authors would like to thank Dan Lee of Hamilton Company for the supply of the PRP-X800 itaconic acid cation column.

References

- [1] C. Sarzanini, E.J. Mentasti, J. Chromatogr. A 789 (1997) 301.
- [2] P.E. Jackson, C.A. Pohl, Trends Anal. Chem. 16 (1997) 393.

- [3] C.A. Pohl, J.R. Stillian, P.E. Jackson, *J. Chromatogr. A* 789 (1997) 29.
- [4] A.I. Elefterov, M.G. Kolpachnikova, P.N. Nesterenko, O.A. Shpigun, *J. Chromatogr. A* 769 (1997) 179.
- [5] P.N. Nesterenko, M.J. Shaw, S.J. Hill, P. Jones, *Microchem. J.* 62 (1999) 58.
- [6] W. Bashir, B. Paull, *J. Chromatogr. A* 907 (2001) 191.
- [7] W. Bashir, B. Paull, *J. Chromatogr. A* 910 (2001) 301.
- [8] W. Bashir, B. Paull, *J. Chromatogr. A* 942 (2002) 73.
- [9] P. Jones, P.N. Nesterenko, *J. Chromatogr. A* 789 (1997) 413.
- [10] Y.J. Seok, K.S. Yang, S.O. Kang, *Anal. Chim. Acta* 306 (1995) 351.
- [11] N.E. Fortier, J.S. Fritz, *Talanta* 34 (1987) 415.
- [12] M.A. Rey, C.A. Pohl, *J. Chromatogr. A* 739 (1996) 87.
- [13] P. Hatsis, C.A. Lucy, *Analyst* 126 (2001) 2113.
- [14] P.N. Nesterenko, P. Jones, *J. Chromatogr. A* 804 (1998) 223.