

Selectivity behaviour of a bonded phosphonate–carboxylate polymeric ion exchanger for metal cations with varying eluent compositions

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Abstract

The chromatographic behaviour of a commercially available ion-exchange stationary phase (the Dionex IonPac CS12A column) is described for a wide range of transition and heavy metal ions with nitric acid eluents containing chloride and nitrate potassium salts. The separation selectivity was found to arise from simultaneous ion-exchange interactions and chelation with the attached carboxylic and phosphonic acid groups. These interactions were investigated by altering the ionic strength and pH of the eluent and also the column temperature. Strong affinity of the stationary phase towards heavy metal ions, in particular bismuth and the uranyl ion was observed at low pH under chelating ion-exchange conditions, with high efficiency separations of other ions including cadmium and lead being possible with short analysis times (~5–15 min). Examples are given of separations obtained using 4-(2-pyridylazo)resorcinol or Arsenazo III as the post-column chromogenic reagents, demonstrating the potential versatility and utility of this stationary phase for heavy metal ion analysis. © 2003 Elsevier Science B.V. All rights reserved.

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1. Introduction

Many novel approaches to stationary phase design for the separation and determination of transition and heavy metal ions in various sample matrices by ion chromatography have been investigated over recent years, as shown in a number of comprehensive reviews [1–4]. Bonded ion-exchange phases, dynamically loaded ion interaction reagents and chelating substrates have all been applied successfully for metal ion analysis.

The column of choice for the ion-exchange separa-

tion of metal ions, especially transition metals, appears to be the IonPac CS5A (Dionex). This pellicular packing (9 µm particles) has an ethylene–vinylbenzene divinylbenzene resin core (55% cross-linking) consisting of two layers of latex particles, functionalised with both alkyl quaternary amine (internal layer) and sulfonic acid groups (outer layer) giving anion- and cation-exchange capacities of 40 and 20 µequivalents per column, respectively. The purpose of having both cation and anion-exchange groups on the resin is to alter the column selectivity in a manner which is dependent on the nature of the complexing agent added to the eluent. Usually either dipicolinic acid (a strong chelator) or oxalic acid (a weaker chelator) is added to the eluent to aid the

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separation of metal ions, and many studies have been undertaken to optimise each system since co-elution can still result dependent upon analyte concentration [5–7]. Various applications, such as the determination of transition and heavy metal ions in various biological, environmental and geological samples have been achieved using this column, often in conjunction with an on-line matrix elimination and analyte pre-concentration step using a small iminodiacetate chelating column [8–10].

The IonPac CS10 column (Dionex), another 55% cross-linked pellicular packing (8.5 μm particles) with a latex coating containing sulfonate groups only and a column ion-exchange capacity of 80 $\mu\text{equivalents}$ has also been used for the separation of particular transition and heavy metal ions in various samples, particularly uranium and thorium [11–13]. Another commercially available column, the IonPac CS12A (Dionex) has yet to be investigated as a suitable stationary phase for transition and heavy metal ion separations. This cation-exchange column was first introduced in 1995 specifically to increase the separation selectivity between the alkali, alkaline earth ions and manganese, and to improve their separation efficiencies using sulfuric or methane-sulfonate eluents. The CS12A column was additionally found suitable for the separation of various amines [14]. It has subsequently been utilised for the determination of alkali and alkaline earth metal ions and ammonium in many challenging matrices including brines/seawater and solvents [15–17]. The resin is highly cross-linked (55%) ethylvinylbenzene–divinylbenzene with grafted carboxylate and phosphonate monomers in a ratio of 5:1. It thus differs from the columns mentioned above in that the ion-exchange groups are attached directly to the substrate rather than via latex particles adsorbed electrostatically onto the substrate surface. The packing has an average particle size of 8.5 μm , and an ion-

exchange capacity of 2800 $\mu\text{equivalents}$, which is significantly greater than that on both the CS5A and CS10 columns. The purpose of the phosphonate group is predominantly to better resolve manganese from magnesium, as manganese is retained more strongly than both magnesium and calcium by this group.

In addition to the ion-exchange interactions occurring between the functional groups on the CS12A column and transition and heavy metal ions, there exists the potential for chelation reactions with the phosphonate and carboxylate ligands. Such chelation might provide a unique pattern of separation selectivity and thus is worthy of investigation. The formation constants of transition metal ions with either maleic acid or ethylphosphonic acid (as the homogeneous analogue of vinylphosphonic acid) are provided in Table 1, and give an indication of the possible retention pattern of these ions on the CS12A column. The modelled $\text{p}K_{\text{a}}$ values corresponding to the phosphonate group on the resin (taken as vinylphosphonic acid) are 2.4 and 7.7, with values of 3.8 and 5.6 given for the carboxylate group (taken as styrene–maleic anhydride) [20]. It should be noted that the ion-exchange selectivity of transition and heavy metals with ion-exchangers containing only phosphonic acid functional groups has not been studied previously. There are some data on the retention behaviour of these metal ions on an aminophosphonate-based chelating ion-exchanger which demonstrated very promising preliminary results, indicative that the phosphonate group might also be a good ligand for metal separations [21,22]. The aim of the present work was therefore to study the separation selectivity of these ions on the CS12A column by varying the ionic strength and pH of the eluent and to determine the suitability of this stationary phase for separating and determining metal cations of environmental interest.

Table 1
Stability constants of complexes of ethylphosphonic and maleic acids with selected metal ions in 0.1 M NaNO_3 [18,19]

Ligand	Mn^{2+}	Zn	Co	Ni	Cd	Cu	Pb	Mg	Ca	Sr	Ba	Be	UO_2
Maleic acid β_1	1.68	2.0	–	2.0	2.3	3.4	3.1	2.30 ^a	2.44 ^a	–	2.30 ^a	4.33	4.46 ^b
Ethylphosphonic acid	2.51	2.67	2.27	2.30	2.94	3.59	–	1.86	1.61	1.35	1.30	6.1 ^a	–

^a Ionic strength=0.

^b Ionic strength=1.

2. Experimental

2.1. Instrumentation

The ion chromatographic system consisted of a Dionex IP25 isocratic pump (Sunnyvale, CA, USA) set to deliver 1 ml min^{-1} , a Waters (Milford, MA, USA) TCM Column Oven connected to a Dionex AS50 auto-sampler with an automated Rheodyne (Cotati, CA, USA) polyether ether ketone (PEEK) liquid six port injection valve fitted with a $100 \mu\text{l}$ PEEK sample loop. The column was an IonPac CS12A with CG12A guard (Dionex). The post-column detection system comprised a Waters Reagent Delivery Module set to deliver the post-column reagent (PCR) at 0.7 ml min^{-1} using compressed nitrogen, a zero dead volume PTFE tee and a $750 \mu\text{l}$ PTFE reaction coil (Dionex). Detection was achieved using an AD20 UV-Vis detector (Dionex).

2.2. Reagents

All reagents were of AnalR grade (BDH, Kilsyth, Australia) with the exception of Arsenazo III, pyrocatechol violet (Sigma, MO, USA), 4-(2-pyridylazo)resorcinol (PAR) (Aldrich, WI, USA), chrome azurol S (Riedel-de Haen, Seelze, Germany) and zinc-EDTA (Fluka, Buchs, Switzerland). Metal standards were prepared using Spectrosol 1000 mg l^{-1} solutions (BDH) with the exception of niobium, thorium, uranium, vanadium(V), hafnium, zirconium (Aldrich), titanium (QCD Analysts, FL, USA), bismuth (Plasma Chem., NJ, USA) and the lanthanides (Light Co., Colnbrook, UK) and stored in polypropylene bottles (BDH).

The post-column reagents used during these studies were 0.15 mM Arsenazo III in 0.5 M acetic acid (with detection at 654 nm) for the lanthanides, 0.15 mM Arsenazo III in 1 M nitric acid for uranium, bismuth, thorium and zirconium (with detection at 654 nm), 0.1 mM PAR, 0.125 M disodium tetraborate and 0.2 M sodium hydroxide (pH 10.5) for the transition metals (with detection at 520 nm), 0.1 mM PAR, 0.2 mM Zn-EDTA and 2 M 28% w/w ammonia for the alkaline earths (with detection at 520 nm), 0.004% pyrocatechol violet in 1 M hexamine (pH 6.8) for aluminium (with detection at 580 nm), 0.008% chrome azurol S in 0.5 M hexamine

(pH 6.5) for beryllium (with detection at 560 nm) and 0.1 mM PAR in 1 M hexamine (pH 6.5) for vanadium, niobium, tantalum, hafnium and titanium (with detection at 520 nm). The eluent consisted of varying concentrations of aqueous inorganic salt as specified, adjusted to the appropriate pH with nitric acid. All reagents and metal ion standards were prepared using ultra-pure Milli-Q water (Millipore, MA, USA).

3. Results and discussion

3.1. Ion-exchange selectivity for transition metal ions

As stated in the introduction, the CS12A column was designed principally to solve the problem of co-elution of manganese ion and the alkaline earth metals. For this reason manganese has been the only transition metal ion for which retention behaviour has been examined to date on this stationary phase. The retention behaviour of other transition metal ions was therefore examined over the range $10\text{--}50 \text{ mM}$ nitric acid, with the results being shown in Fig. 1. The elution order did not alter with increasing pH, being $\text{Pb(II)} > \text{Cu(II)} > \text{Cd(II)} > \text{Ni(II)}/\text{Co(II)}/\text{Zn(II)} > \text{Mn(II)} > \text{Fe(II)}$, indicative that iron present in any sample would be likely to interfere with the alkaline earth metals, with nickel, cobalt and zinc ions also being potential interferents since these

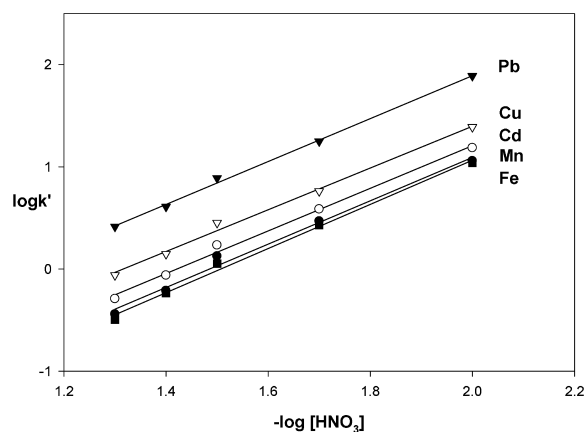


Fig. 1. Effect of [nitric acid] on the retention of selected transition metal ions with the CS12A column. Other eluent conditions: 30°C , 1 ml min^{-1} . Detection conditions as given in the text.

species were retained only slightly more strongly. The observed retention order for transition metal ions corresponded to the stability constants of metal complexes between these ions and ligands having carboxylate functionalities (Table 1), with the exception of lead. Lead was very strongly retained on the CS12A column when ion-exchange interactions were dominant, having a retention time of about 65 min at 40 mM acid concentration. Previous studies [23] have shown that lead was retained more weakly than copper on a column having only carboxylic acid functional groups. This suggested that the strong retention of this metal ion on the CS12A column was a consequence of the phosphonic acid groups present on the stationary phase.

There are two considerations that could be of interest regarding possible applications of the IonPac CS12A column. The first of these is the increased affinity towards heavy metal ions over alkali and alkaline earth ions. A separation of four metal ions, including the environmentally significant lead and cadmium ions is given in Fig. 2. Lead was retained very strongly under the isocratic elution conditions used. The second consideration is that the symmetry and efficiency of the chromatographic peak for nickel is good, which is normally not the case under isocratic ion-chromatographic separation conditions with chelating ligands [3]. However, a disadvantage of pure ion-exchange separation on this column was

the co-elution of nickel, cobalt and zinc ions, which persisted over all of the eluent acid concentrations studied.

3.2. Effects of ionic strength and pH of the eluent

The effect of ionic strength on the retention of these transition metals was determined. In previous studies eluent ionic strength has been shown to influence the dominant retention mechanism occurring when using ion-exchange stationary phases with chelating groups [3]. In a low ionic strength eluent, both the carboxylate and phosphonate groups will play a role in the ion-exchange retention of metal ions through their ionised hydroxyl moieties, in accordance with the modelled pK_a data given earlier, in addition to chelation interactions predicted by Table 1. The effect of ionic strength (through addition of potassium nitrate to the eluent) on the retention of selected transition metals is shown in Fig. 3, which shows that retention was reduced progressively as the added K^+ ions competed effectively for the ion-exchange sites of the CS12A resin. The retention behaviour of nickel ions (data not shown) was similar to that of zinc ions, whilst iron(II) and manganese behaved in a manner similar to cobalt ions. From these data, it was apparent that an eluent ionic strength of 0.5 M was sufficient to almost completely suppress any ion-exchange inter-

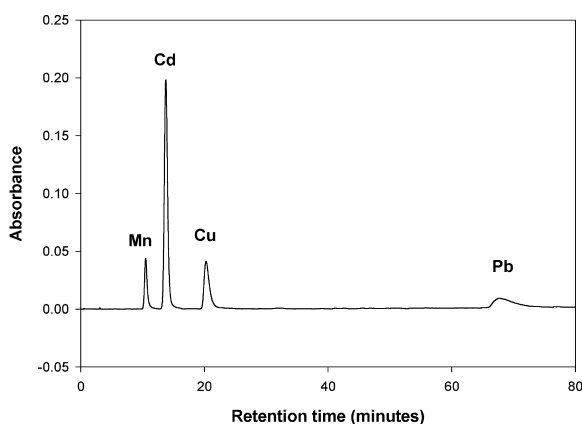


Fig. 2. Separation of manganese (0.5 mg l^{-1}), cadmium (5 mg l^{-1}), copper (1 mg l^{-1}) and lead (5 mg l^{-1}) on the CS12A column. Eluent conditions: 40 mM nitric acid, 30 °C, 1 ml min^{-1} . Detection conditions as given in the text.

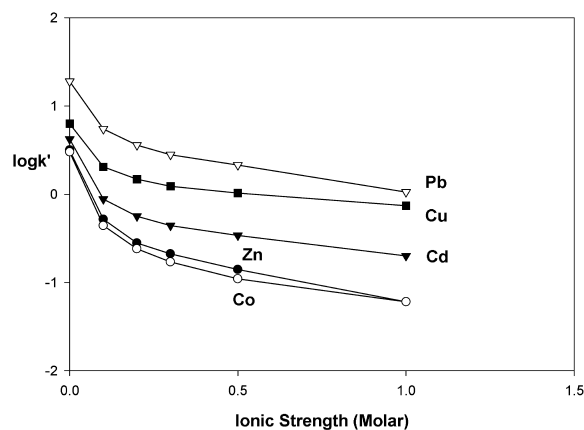


Fig. 3. Effect of ionic strength (on addition of potassium nitrate) on the selectivity and retention of selected metal ions with the CS12A column. Other eluent conditions: 20 mM nitric acid, 30 °C, 1 ml min^{-1} . Detection conditions as given in the text.

actions on the column and to ensure that chelation was the dominant retention mechanism. This is in agreement with previous research [3].

With chelating substrates, pH can be used as a convenient factor to manipulate and optimise the degree of retention through alterations in the degree of metal complex formation. The effect of eluent pH (0.5–20 mM nitric acid) on the retention of selected transition metals is given in Fig. 4. The elution order under chelating conditions was Pb(II)>Cu(II)>Cd(II)>Zn(II)>Ni(II)>Co(II)>Mn(II)/Fe(II), which did not alter with changes in pH. Of interest was the improved separation between zinc, nickel, cobalt and manganese ions, which could be baseline separated from each other and also from the alkaline earth metal ions (Fig. 5). This separation could not be accomplished by ion-exchange alone. It was also noteworthy that peak shapes for nickel and cobalt ions were good. A separation of manganese, cadmium, copper and lead ions is shown in Fig. 6, and comparison with Fig. 2 reveals that this separation was faster than that accomplished by ion-exchange alone and the observed peak shapes in Fig. 6 were good for a chelating ion-exchange separation. Previous research has indicated that with some chelating groups, complex dissociation is slow and this leads to peak profiles showing significant tailing.

The separation selectivity of metal ions on the CS12A column was different to that exhibited by a

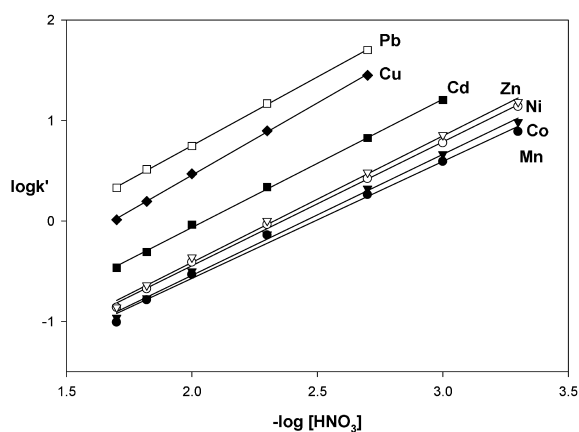


Fig. 4. Effect of eluent pH on the retention of selected transition metal ions with the CS12A column. Other eluent conditions: 0.5 M potassium nitrate, 30 °C, 1 ml min⁻¹. Detection conditions as given in the text.

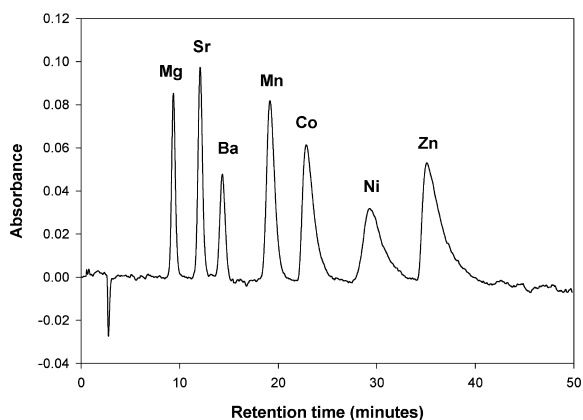


Fig. 5. Separation of magnesium (1 mg l⁻¹), strontium (5 mg l⁻¹), barium (5 mg l⁻¹), manganese (5 mg l⁻¹), cobalt (5 mg l⁻¹), nickel (5 mg l⁻¹) and zinc (10 mg l⁻¹) on the CS12A column. Eluent conditions: 0.5 M potassium nitrate, 0.5 mM nitric acid, 30 °C, 1 ml min⁻¹. Detection conditions as given in the text.

fabricated aminophosphonic acid silica-based column investigated previously [21]. Under conditions where chelation with two oxygen atoms occurred (O,O chelation) at pH 1, the elution order was Mn(II)>Cd(II)>Pb(II)>Cu(II)>Zn(II)>Co(II)>Ni(II), changing to Cu(II)>Pb(II)>Cd(II)>Zn(II)>Ni(II)>Mn(II) with increasing pH and the introduction of additional chelation through the amino group [21]. The elution order was also different to that shown by an O,O chelating itaconic acid resin with only maleic

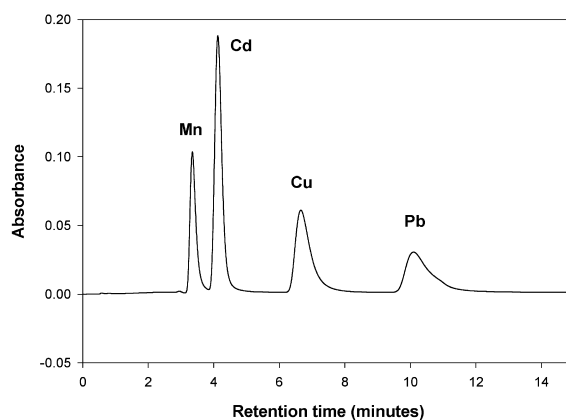


Fig. 6. Separation of manganese (0.5 mg l⁻¹), cadmium (2 mg l⁻¹), copper (1 mg l⁻¹) and lead (4 mg l⁻¹) on the CS12A column. Eluent conditions: 0.5 M potassium nitrate, 15 mM nitric acid, 30 °C, 1 ml min⁻¹. Detection conditions as given in the text.

acid groups present, in this instance being $\text{Cu(II)} > \text{Pb(II)} > \text{Co(II)} > \text{Zn(II)} > \text{Cd(II)} > \text{Mn(II)}$ in the presence of a high ionic strength eluent (potassium nitrate) [23]. This would infer that the unique selectivity observed with the CS12A column resulted from the large concentration of carboxyl groups present (given the retention order is similar to the stability constants of metals with maleic acid given in Table 1), in addition to the presence of the phosphonate ligand which contributed chiefly to the strong retention of lead ions. Peak shapes were also much sharper with the CS12A column in comparison with the recently studied itaconic acid substrate [23], noticeably so for Co(II) for which the broad peaks associated with the itaconic acid column were indicative of slow dissociation kinetics of complexes formed with the maleic acid groups. The addition of the phosphonate functional groups appears to provide much improved kinetics, especially taking into account the good peak shapes encountered previously with the aminophosphonate ligand [21].

Retention behaviour of the alkaline earth ions was also examined on the CS12A stationary phase under chelating ion-exchange conditions. As mentioned in the Introduction, the retention of these species under ion-exchange conditions has been studied extensively, with an elution order of $\text{Ba(II)} > \text{Sr(II)} > \text{Ca(II)} > \text{Mg(II)}$ being observed [14]. The same elution order was shown by chelation ion-exchange (Fig. 7), with the exception that at approximately pH 2.5, calcium became more strongly retained than strontium, giving an elution order of $\text{Be(II)} > \text{Ba(II)} > \text{Ca(II)} > \text{Sr(II)} > \text{Mg(II)}$. This change coincided with the deprotonation of the first phosphonate oxygen atom ($\text{p}K_1 = 2.4$), leading to concomitant changes to the structure of ion-exchange sites at the surface of the CS12A resin. As anticipated, the small but relatively highly charged beryllium ion was retained strongly but the observed peak tailed. Manganese ion has been included in Fig. 7 to illustrate potential interferences between this ion and the alkaline earth metal ions.

3.3. Effect of Cl^- ions in the eluent

Chloride, present in many environmental matrices including seawater and brines, can have important consequences concerning the elution of metal ions

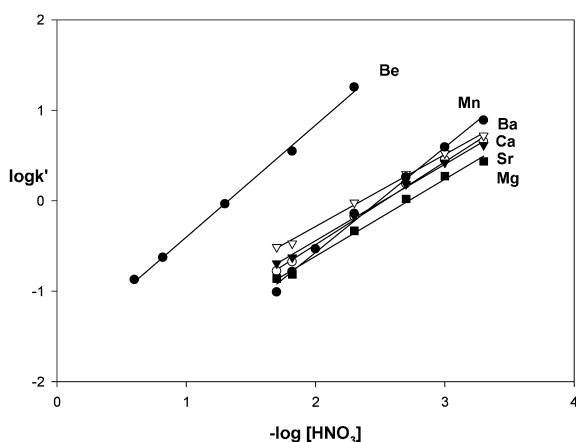


Fig. 7. Effect of eluent pH on the retention of selected alkaline earth metal ions on the CS12A column. Other eluent conditions: 0.5 M potassium nitrate, 30 °C, 1 ml min⁻¹. Detection conditions as given in the text.

using chelating substrates as a result of the formation of chloro-complexes, most notably with lead and cadmium ions. The effect of Cl^- in the eluent was therefore considered. The formation constants ($\log K_1$ values at 0.5–1 M ionic strength and 25 °C) of some transition metal ions with Cl^- are $\text{Pb(II)} = 0.9$, $\text{Cd(II)} = 1.35$, $\text{Zn(II)} = 0.11$, $\text{Mn(II)} = 0.04$, $\text{Co(II)} = -0.05$, $\text{Ni(II)} = 0.00$, $\text{Cu(II)} = 0.09$ (2 M ionic strength) [24]. The ionic strength of the eluent was varied from 0 to 0.2 M using potassium chloride, and as anticipated the retention for both Pb(II) and Cd(II) was reduced significantly in comparison with a potassium nitrate eluent at an identical acid concentration (20 mM). This effect was most noticeable for Cd(II) which became the least retained ion. No other selectivity changes were observed, the elution order being $\text{Pb(II)} > \text{Cu(II)} > \text{Zn(II)} > \text{Ni(II)} > \text{Co(II)} > \text{Fe(II)} > \text{Mn(II)} > \text{Cd(II)}$. The effect of eluent pH on the retention of these ions in a chloride eluent is given in Fig. 8, which demonstrates improved selectivity between Fe(II) and Mn(II) in comparison with a potassium nitrate eluent.

3.4. Influence of column temperature

The effect of temperature as a parameter to improve resolution and to impart selectivity changes on the CS12A column has been investigated previ-

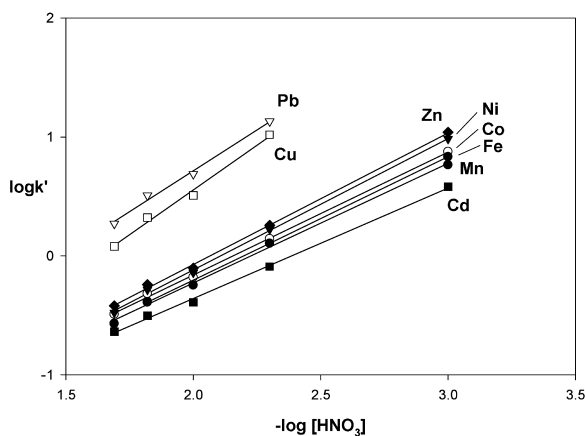


Fig. 8. Effect of eluent pH on the retention of selected transition metal ions on the CS12A column. Other eluent conditions: 0.2 M potassium chloride, 30 °C, 1 ml min⁻¹. Detection conditions as given in the text.

ously under pure ion-exchange conditions using methanesulfonic acid eluents [14,25]. It was shown that when ion-exchange was the dominant retention mode, an increase in column temperature resulted in a decrease in retention for both the alkali and alkaline earth metal ions. Under complexation conditions using stationary phase ligands, an elevation in temperature has been shown to increase analyte retention due to an entropy effect [3]. This behaviour has recently been illustrated with the itaconic acid column with attached maleic acid groups, for transition and alkaline earth metal ions [23].

The effect of temperature on the retention of selected transition and alkaline earth metal ions with a chloride-based eluent on the CS12A column is shown in Fig. 9. A nitric acid concentration of 0.9 mM was chosen as this gave adequate resolution of many transition metal ions (as shown by Fig. 8). However, at this pH the alkaline earth metals were retained strongly using a chloride based eluent, with some co-elution occurring at ambient temperature (25 °C). As expected, increasing the temperature resulted in an increased retention of all the metals examined, although for Sr(II) and Ba(II) this increase was negligible over the range studied (25–55 °C). This might possibly have resulted from opposing influences of simultaneous ion-exchange and complexation modes of retention for these ions.

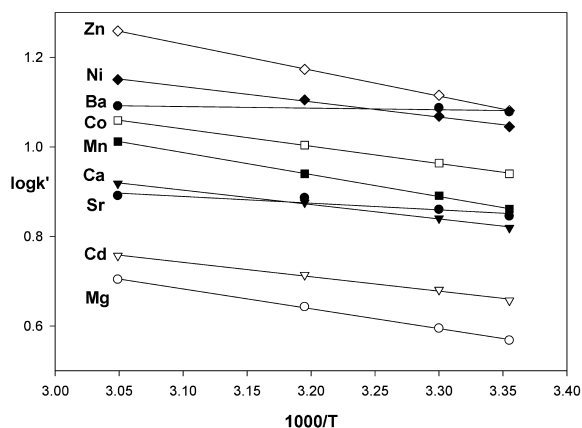


Fig. 9. Influence of column temperature on the retention of selected metal ions on the CS12A column. Eluent conditions: 0.2 M potassium chloride, 0.9 mM nitric acid, 1 ml min⁻¹. Detection conditions as given in the text.

As mentioned previously, increasing the column temperature results in an increase in retention when complexation is dominant, and a decrease in retention when ion-exchange interactions are dominant. According to Table 1, complex formation between Sr(II) and Ba(II) and the phosphonic acid ligand is the weakest for all the metal ions examined, and chelation is also weak with the maleic acid groups, so that ion-exchange interactions can be expected to affect retention. Nevertheless, changes in separation selectivity were noted, with Ca(II) becoming more strongly retained than Sr(II), and Ba(II), initially co-eluting with Zn(II) at 25 °C becoming more weakly retained than both Ni(II) and Zn(II) as the temperature increased. Temperature could therefore be used to optimise selectivity, as illustrated by the separation of eight metal ions at 50 °C given as Fig. 10. This figure also illustrates the weak retention of Cd(II) with a chloride based eluent.

The effect of temperature on the retention of these metals with a nitrate-based eluent was also examined to ascertain whether Sr(II) and Ba(II) behaved similarly. Slopes of plots of $\log k'$ vs. temperature for each metal ion with both potassium chloride and nitrate salt eluents are given in Table 2. This shows that both Sr(II) and Ba(II) exhibited reduced slope values in comparison with other metal ions in the nitrate-based eluent. This reduction was less than that with the chloride-based eluent and over the

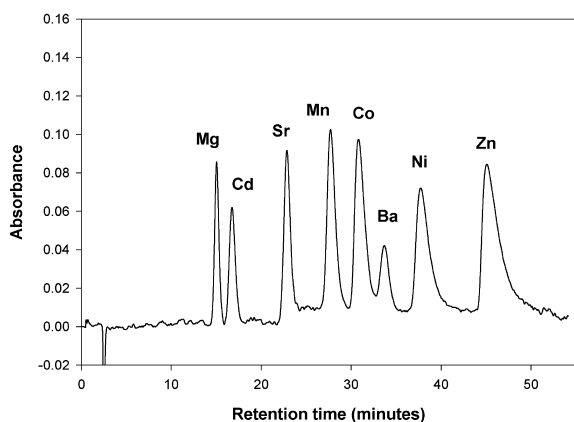


Fig. 10. Separation of magnesium (1 mg l^{-1}), cadmium (5 mg l^{-1}), strontium (5 mg l^{-1}), manganese (5 mg l^{-1}), cobalt (5 mg l^{-1}), barium (5 mg l^{-1}), nickel (5 mg l^{-1}) and zinc (10 mg l^{-1}) on the CS12A column. Eluent conditions: 0.2 M potassium chloride, 0.9 mM nitric acid, 50°C , 1 ml min^{-1} . Detection conditions as given in the text.

temperature range studied, and no changes in retention order were noted. The slopes for the other metal ions were fairly similar using both eluents.

3.5. Metal retention on the guard column alone

A range of strongly retained metal ions (by chelating groups) was investigated using the CG12A guard column as stationary phase in order to obtain retention data in the shortest possible time and to investigate the utility of this guard column for analytical separations. Fig. 11 shows the retention data obtained, from which it is interesting to note the change in selectivity between bismuth and the uranyl

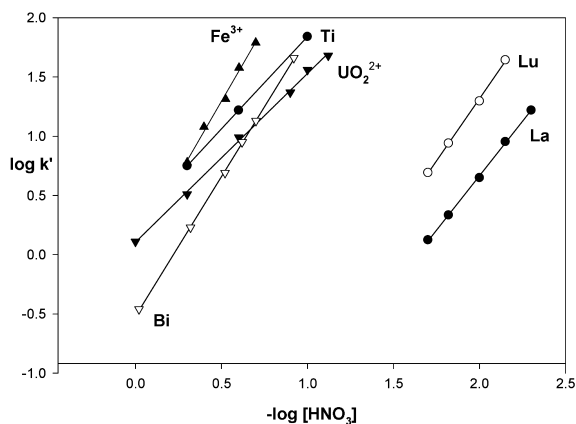


Fig. 11. Effect of eluent pH on the retention of selected metal ions with the CG12A column. Other eluent conditions: 0.5 M potassium nitrate, 30°C , 1 ml min^{-1} . Detection conditions as given in the text.

ion at approximately pH 0.6. Slopes for the lanthanide ions were close to -2 , uranyl ion -1.5 , titanium -1.5 , iron(III) -2.5 , bismuth(III) -2.3 and transition metal ions were all approximately -1.2 using a potassium nitrate eluent. These values were less than those predicted from ion-exchange theory and again indicate that complexation was occurring with the deprotonated and neutral -P=O and -C=O groups on the resin surface, to a degree dependent upon the metal ion and its degree of hydrolysis.

Titanium, iron (III), bismuth and uranyl ion were all strongly retained on the guard column and bismuth and uranyl could be separated with relatively good peak shapes, whilst titanium(III) and iron(III) gave broad, tailing peaks. In addition to these ions, aluminium(III) was weakly retained but tailed badly, thorium, hafnium and zirconium were fully retained, even at an acid concentration of 1 M , whilst vanadium (V), tantalum and niobium were un-retained over a wide pH range. The lanthanides were well retained, and have been examined in far more detail on this substrate elsewhere [26]. They are however, more weakly retained than the uranyl ion and bismuth, which should allow their separation in geological and environmental samples.

The effect of temperature on the CG12A guard column was investigated briefly for the uranyl ion and was found to have a minimal effect over the range $20\text{--}50^\circ\text{C}$.

Table 2

Derived slopes for selected metal ions as a function of temperature vs. $\log k'$

Metal	1 (chloride)	2 (nitrate)
Magnesium	-0.44	-0.44
Strontium	-0.15	-0.24
Calcium	-0.32	-0.31
Barium	-0.08	-0.11
Manganese	-0.49	-0.53
Nickel	-0.34	-0.36
Cobalt	-0.39	-0.39
Zinc	-0.58	-0.68

Eluent conditions 1: 0.2 M potassium chloride, 0.9 mM nitric acid, 2: 0.5 M potassium nitrate, 0.9 mM nitric acid, 1 ml min^{-1} .

4. Conclusions

The Dionex CS12A column packing has been shown to be a versatile and efficient stationary phase for the separation of many metal ions under chelating ion-exchange conditions. The kinetics of complexation of metal ions with the phosphonate and carboxylate groups under isocratic eluent conditions were improved in comparison with previously investigated chelating substrates. Subsequent work is currently under way to apply this column to real sample analyses for metal ions in complex sample matrices, including seawater.

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