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Determination of trace alkaline earth metals in brines using chelation ion chromatography with an iminodiacetic acid bonded silica column

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Abstract

The chromatographic behaviour of alkaline earth metals on iminodiacetic acid bonded silica was studied. It was found that the ionic strength of the eluent greatly affected both retention time and selectivity by controlling the extent to which either simple ion exchange or surface complexation was responsible for retention. With a 0.1 M KNO₃ eluent, the retention order was Mg(II), Sr(II), Ca(II) and Ba(II), indicating a strong contribution to retention from ion exchange. However, when using a 1.5 M KNO₃ eluent, Ba(II) was found to elute first, indicating complexation to be more dominant under these conditions (pH 4.2). The effect of the ionic strength of the sample was also studied and it was found that by matching the eluent cation with that of the sample matrix, efficient separations of alkaline earth metals in 1.0 M NaCl and KCl brines could be obtained without matrix system peaks. Using post-column reaction with *o*-cresolphthalein complexone, trace levels of Ca(II) and Mg(II) were determined in medicinal NaCl saline solution and laboratory-grade KCl. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

The determination of trace metals in complex sample matrices using ion chromatographic methods has received considerable attention in recent years. Simple ion-exchange chromatography is ideal for the determination of alkali and alkaline earth metal ions, but only if the sample is relatively low in ionic strength. If the ionic strength is too high, the matrix ions swamp the ion-exchange sites (a process known

as self-elution), seriously affecting the separation efficiency. Thus the direct analysis of important samples, such as surface saline waters, biological/geological digests, and natural/industrial brines can be extremely difficult by conventional ion-exchange chromatography, with many published methods requiring matrix elimination/preconcentration or large sample dilutions before injection.

One such system which has been developed by the Dionex Corporation, involves the preconcentration of trace metal ions onto a chelating mini-column, followed by their elution onto a strong ion-exchange concentrator column and finally their separation on a standard ion-exchange analytical column [1–9]. This

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methodology has been applied to a range of high-ionic-strength samples such as seawater [1–3], biological fluids and tissue digests [1,4], geological digests [5], drinking and surface waters [6,7], inorganic reagents and organic solvents [8] and industrial brines [9]. However, despite the obvious versatility of the above system, it is evident that the equipment required is rather complex, involving a combination of a number of concentrator and separator columns, pumps and switching valves.

A better solution to the analysis of these types of samples would be the development of stationary phase materials which exhibit the correct selectivity to allow the injection of high-ionic-strength samples directly, without any on-line pretreatment. One approach, which has been extensively developed over the previous decade, is the use of high-performance chelating stationary phases. These exhibit unique selectivity compared to simple ion-exchange resins, showing little or no affinity for alkali metals, whilst at the same time being capable of producing high-performance separations of many di- and trivalent metal ions (depending upon the type of functional group). Two recent reviews on so-called “high-performance chelation ion chromatography” have been compiled by Jones and Nesterenko [10] and Paull and Haddad [11] which detail the types of stationary phase materials available, how these materials have been produced and the applications which have been developed.

Iminodiacetic acid bonded silica (IDA-silica) is one such material and has been investigated as a stationary phase for the separation of metal ions. Much of this work has focused on the separation of transition and heavy metal ions [12–15] and more recently the lanthanide series metals [16,17], although several workers have also investigated the potential of IDA-silica for the separation of both alkali and alkaline earth metals [18–20]. Elefterov et al. [18] studied the chromatographic behaviour of alkali and alkaline earth metal ions on IDA-silica using mineral and organic acid eluents. Retention of alkali metals was found to be predominantly due to simple ion exchange, whereas retention of the alkaline earth metals was thought to be due to a combination of ion exchange and complexation. A mixed eluent containing perchloric acid and a complexing organic acid was used to obtain a simulta-

neous separation of alkali and alkaline earth metals in a single run. Later work by Kolpachnikova et al. [19] studied the effect of temperature on the retention of alkali and alkaline earth metals on selected aminocarboxylic acid bonded silica columns. It was shown that IDA-silica behaved somewhat differently to the other polyfunctional ion exchangers studied, again indicating that a dual retention mechanism was responsible for the changes in selectivity shown.

Application of IDA-silica columns to the analysis of alkaline earth metals in complex sample types has been rather limited. Elefterov et al. [18] applied their developed method to the analysis of simple drinking and mineral waters, whilst Voloschik et al. [20] developed a method for the determination of Be(II) in rock digests using ion chromatography with an IDA-silica column. This current paper looks at the use of IDA-silica as a stationary phase for the separation of alkaline earth metals in high-ionic-strength samples, such as chloride brines. It also further investigates the true retention mechanism taking place within the system and illustrates the unique and versatile selectivity IDA-silica offers for the analysis of alkaline earth metal ions. A potential application of the method described is the analysis of trace levels of Ca(II) and Mg(II) in concentrated solutions of NaCl and KCl. This is of great interest to the chlor-alkali industry, where membrane poisoning in chlor-alkali cells can result from concentrations of Ca(II) and Mg(II) above 50 µg/l. A number of workers have developed methods for this particular analysis, however, each contains a pre-concentration/matrix elimination step [9,21,22]. The method described here is for the determination of Ca(II) and Mg(II) in high-ionic-strength samples, through direct injection onto the analytical IDA-silica column with sensitive and selective post-column reaction detection.

2. Experimental

2.1. Instrumentation

A Dionex Model GPM2 gradient pump module (Sunnyvale, CA, USA) was used to deliver the eluent (1.0 ml/min). A manual sample injection valve, Model 7125 (Rheodyne, Cotati, CA, USA), fitted

with a 100- μ l injection loop was used for introduction of the samples. The IDA-silica packed analytical column (8 μ m particle size, 130 Å pore size, 250 \times 4.0 mm I.D.) used was supplied by BioChemMack (Moscow, Russia). A pressure-driven Dionex reagent delivery module was used for introduction of the post-column reagent (1.5 ml/min), which was mixed at room temperature with the eluent using a 0.5 m polyether ether ketone (PEEK) reaction coil (0.25 mm I.D.). A Model SPD-6AV Shimadzu UV-Vis detector (Kyoto, Japan) was used at 572 nm to monitor the resultant chromatograms. These were recorded using Dionex AI450 chromatographic software.

2.2. Reagents

The eluent and post-column reagent (PCR) were prepared using deionised water from a Millipore Milli-Q water purification system (Bedford, MA, USA). The PCR ligand, *o*-cresolphthalein complexone (*o*-CPC), was purchased from Sigma-Aldrich (Gillingham, UK) and used without further purification. Potassium nitrate and boric acid was obtained from Merck (Darmstadt, Germany). Sodium nitrate was purchased from Riedel-de Haen (Sleeze-Hannover, Germany) and lithium chloride, sodium chloride and potassium chloride were all obtained from Fluka (Buchs, Switzerland). Final eluent conditions for the analysis of samples were 1.0 M KNO₃ or NaNO₃ adjusted to pH 4.9 using dilute HNO₃. The post-column reagent solution was 0.25 M boric acid, 0.3 mM *o*-CPC adjusted to pH 10.4 using NaOH. All 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. Discussion

3.1. The effect of eluent ionic strength

With IDA functionalised stationary phases both the eluent pH and ionic strength are known to play vital roles in governing which is the dominant

retention mechanism taking place within the system. In the case of silica-based substrates it has been shown that when using low-ionic-strength acidic eluents such as mineral acids, ion exchange is the dominant retention mechanism for both alkali and alkaline earth metal ions [18,19]. This ion exchange capacity originates from both residual silanols and other active hydroxy groups, as well as the attached carboxylic acid groups. At low pH (<pH 4–5) complexation of alkaline earth metal ions plays only a minor role in retention and this can be clearly seen from the selectivity obtained by Nesterenko and co-workers [18,19] when using simple perchloric acid eluents, namely Mg(II)<Ca(II)<Sr(II)<Ba(II), which is the same as that obtained on weak carboxylic acid cation-exchange resins [23]. If IDA-silica is to be applied to high-ionic-strength samples such ion exchange effects have to be minimised so that complexation is the dominant retention mechanism, as it is complexation that offers the desired selectivity. In previous work using IDA-based chelating stationary phases KNO₃ has been found to be a suitable eluent and ionic strength modifier due to its relative high purity and low cost [10]. Therefore, the effect of KNO₃ concentration upon selectivity for alkaline earth metals was investigated here.

The results obtained from varying the concentration of KNO₃ over the range 0.1 to 1.0 M are plotted in Fig. 1, with a number of the resultant chromatograms shown in Fig. 2 (for simplicity, during the following experiments eluents were adjusted to pH 4.2 using dilute HNO₃, although it is recognised that at this pH such an eluent would have

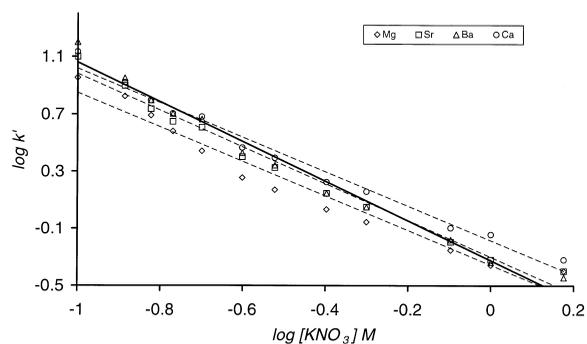


Fig. 1. Plot of $\log k'$ vs. $\log [KNO_3]$ for alkaline earth metal ions on the IDA-silica column. Other conditions: eluent pH 4.2 (HNO₃).

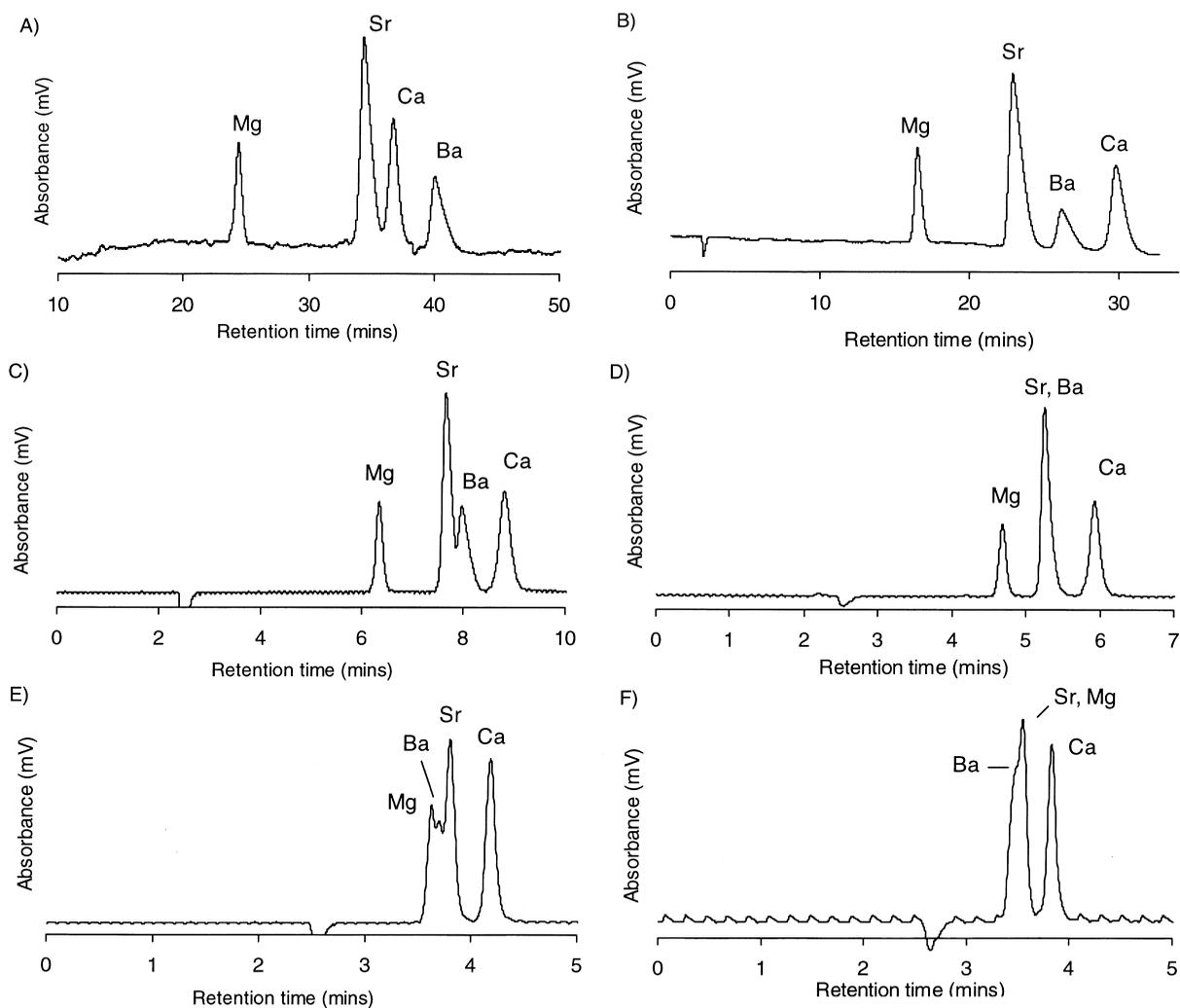


Fig. 2. Separations of alkaline earth metal ions using the IDA-silica column with (A) 0.1 M, (B) 0.2 M, (C) 0.3 M, (D) 0.5 M, (E) 1.0 M and (F) 1.5 M KNO_3 eluent. Other conditions: eluent pH 4.2 (HNO_3).

very little buffering capacity for real samples). From the retention data obtained a number of conclusions can be drawn. Firstly, at 0.1 M KNO_3 the selectivity shown is not typical of either simple ion exchange or chelation, but in fact a combination of both. However, it is clear that ion exchange is the dominant retention mechanism under these conditions, as the selectivity shown matches quite closely to that expected from simple ion exchange on carboxylic acid exchangers, here $\text{Mg(II)} < \text{Sr(II)} < \text{Ca(II)} < \text{Ba(II)}$. This is supported by the known stability constant data available for IDA-alkaline earth metal

complexes [0.1 M KNO_3 , 25°C, Mg(II) $K_1=2.94$, Ca(II) $K_1=2.59$, Sr(II) $K_1=2.23$, Ba(II) $K_1=1.67$] which indicates interaction should only be due to ion exchange and not complexation at $\text{pH} < 5-5.5$ [12,24]. However, as can be seen in Fig. 2 the retention of Ca(II) is unusually high, indicating that some degree of complexation may be responsible for this increased retention of Ca(II) compared to the remaining alkaline earth metal ions. This would appear to contradict the above stability constant data, however, as can be seen from Fig. 2B–F, Ca(II) elutes last under higher ionic strength eluent con-

ditions indicating the strongest degree of complexation. This is supported through comparison of the slopes of linear regression lines fitted to the retention data shown in Fig. 1. The slopes were as follows; $\text{Ca(II)} = -1.20$, $\text{Mg(II)} = -1.21$, $\text{Sr(II)} = -1.28$ and $\text{Ba(II)} = -1.38$. It is clear from these results that Ca(II) is least affected by eluent ionic strength, indicating complexation is the dominant mechanism, whereas Ba(II) is most affected by ionic strength, thus indicating ion exchange is dominant. The quite dramatic transition from last eluting ion to first eluting ion shown by Ba(II) is a clear illustration of how the ion exchange capacity of IDA-silica can be effectively “switched off” through use of high-ionic-strength eluents.

3.2. The effect of eluent pH

The effects of increasing the eluent pH using both a (A) 1 M KNO_3 eluent and (B) a 0.5 M KNO_3 eluent are shown in Fig. 3. Similar responses were obtained using both eluents, although as expected retention times were greater with the 0.1 M eluent due to the added contribution to retention from ion exchange. Once again Ca(II) exhibited differing behaviour to the remaining alkaline earth metal ions, showing a rapid increase in retention at approx. pH 5 and above. It is unclear why Ca(II) should show such differing selectivity to Mg(II) when using non-complexing eluents, particularly when considering the similar stability constant data for the IDA complexes in solution, where in fact the Mg(II) complex is slightly higher [24]. However, it is clear from the Fig. 3 that with both eluents complexation begins to dominate retention at $>\text{pH } 5$ for Ca(II) and $>\text{pH } 6$ for the remaining metal ions (eluent conditions were kept below pH 6.8 as the stationary phase was silica based). This rather unusual selectivity is illustrated in Fig. 4, where the chromatogram shows the baseline separation of Mg(II) , Ba(II) and Sr(II) in under 7 min, whilst Ca(II) is retained for 25 min. The chromatogram was obtained using a 0.5 M KNO_3 eluent (pH 5.9). Taking Fig. 4 together with Fig. 2A and B, it can be seen that baseline separations of the four alkaline earth metals can be achieved, each exhibiting different selectivity, without using a complexing eluent. This shows the clear

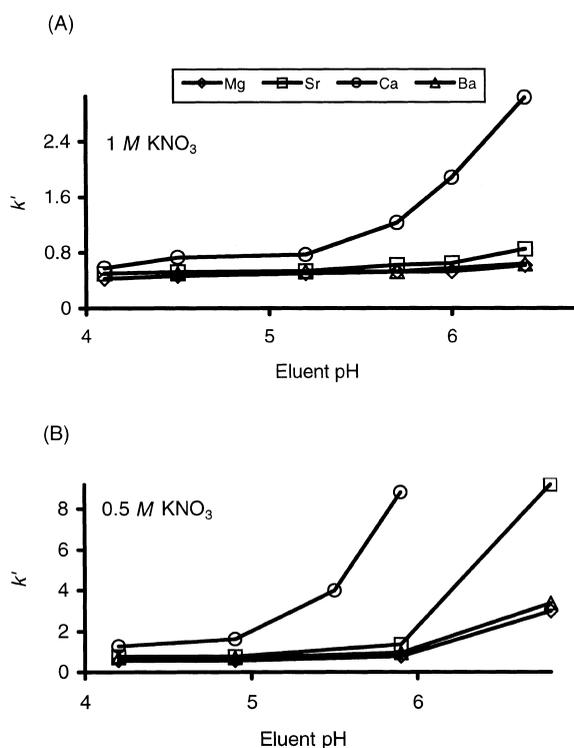


Fig. 3. Plot of (A) k' vs. eluent pH for alkaline earth metal ions on the IDA-silica column using a 1.0 M KNO_3 eluent, and (B) k' vs. eluent pH for alkaline earth metal ions on IDA-silica using a 0.5 M KNO_3 eluent.

advantages to be had from using the IDA-silica column for the separation of this group of metal ions compared to a simple cation exchanger.

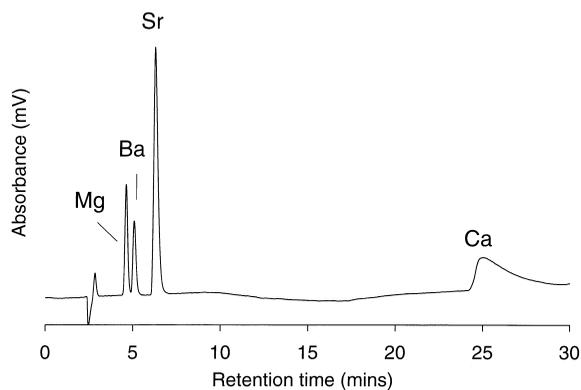


Fig. 4. Separation of alkaline earth metal ions on the IDA-silica column using a 0.5 M KNO_3 eluent, adjusted to pH 5.9 using HNO_3 .

3.3. The effect of column temperature

Column temperature is known to affect ion-exchange chromatography in a somewhat unpredictable manner, depending upon the type of ion exchange material used. Increased column temperature can lead to increased diffusion rates into the ion exchange matrix and thus increased efficiency and stationary phase interaction [23]. In pure ion exchange this effect is relatively poorly documented, with temperature having little effect upon selectivity for metal ions when using sulfonated cation exchangers [19]. However, carboxylic acid type ion exchangers have been shown to behave differently due to their complexation properties. In their recent review, Jones and Nesterenko state that as the “chelate effect” is predominantly an entropy effect, surface complexation will result in a positive increase in entropy and so the change in Gibb’s free energy with temperature will be negative. If temperature is increased, the change in Gibb’s free energy will become even more negative and so the equilibrium constant for the complex being formed will become bigger, hence an increase in retention. Jones and Nesterenko state that with this in mind, if complexation is purely responsible for retention, an increase in temperature should result in an increase in retention [10].

With IDA-silica the effect of temperature upon selectivity is still somewhat unclear. Its effect will be dependent upon the exact combination of retention mechanisms taking place, which itself is dependent upon the ionic strength, pH and complexing or non-complexing nature of the eluent. Kolpachnikova et al. [19] looked at the effects of temperature upon the retention of alkali and alkaline earth metals on IDA-silica and found that under acidic non-complexing conditions, retention of alkaline earth metals actually decreased with an increase in column temperature. However, at the pH of the eluent used in the Kolpachnikova et al. study, namely pH 2.7, it was clear that complexation was not playing a role in retention. Here, the effect of temperature was investigated using a 0.1 M and a 1.0 M KNO_3 eluent at pH 4.1. Fig. 5 shows the results obtained with respect to the retention of Mg(II) and Ca(II). It is evident from the results that temperature effects upon selectivity are dependent upon eluent conditions, here the eluent

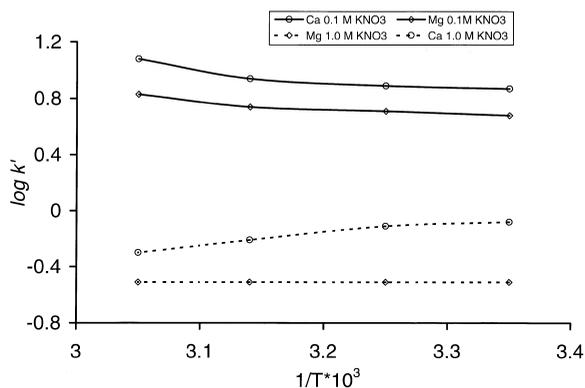


Fig. 5. Plot of $\log k'$ vs. $1/T \cdot 10^3$ for Ca(II) and Mg(II) on the IDA-silica column using 1.0 M and 0.1 M KNO_3 eluents. Other conditions: eluent pH 4.1 (HNO_3).

ionic strength. There is a clear increase in retention of both Mg(II) and Ca(II) with temperature when using the 0.1 M KNO_3 eluent. This in itself is the opposite effect to that shown by Kolpachnikova et al. However, even more unusual is that when using the 1.0 M KNO_3 eluent, where complexation should play a more dominant role in retention, there is an apparent decrease in the retention of Ca(II), whereas Mg(II) remains unaffected. Once more this is the opposite response to that expected, although it again indicates that the exact retention mechanism responsible for the retention of Ca(II) differs considerably to that for Mg(II).

From the above results it is noticeable that there is a distinct change in retention mechanism taking place with increasing ionic strength. However, the responses to changes in column temperature do not correspond to those expected from either pure ion exchange or pure chelation. It seems clear, as mentioned previously, that under this range of eluent conditions a dual retention mechanism is indeed taking place with the dominance of ion exchange or chelation being dependent upon pH and/or ionic strength. Therefore, it can only be concluded here that the effects shown are characteristic of IDA-silica at this particular pH with KNO_3 eluents. Further work is obviously required to fully understand the full effects of temperature upon such a system. However, here it was clear that although temperature could be used to change retention times slightly, it did not change elution orders or greatly improve

efficiency and so was neglected for the remainder of the study.

3.4. The effect of sample matrix

As this study aimed to develop simple methodologies for the analysis of alkaline earth metal ions in high-ionic-strength samples, it was important to determine the real effects of the sample matrix upon the separation achieved and the correct choice of eluents to use with each particular sample. If the contribution to retention from ion exchange is minimised through the use of a high-ionic-strength eluent, the ionic strength of the sample will have less effect upon retention and efficiency. However, even with a high-ionic-strength eluent, there remains a noticeable matrix effect upon the separation of Mg(II) and Ca(II) when using the IDA-silica column. Fig. 6 shows the overlaid separations of 1 mg/l Mg(II) and Ca(II) standards prepared in pure water and 1.0 M KCl using a 1.0 M KNO₃ eluent, adjusted to pH 4.9. Two observations can be made from Fig. 6. Firstly, there is a lack of any system peak from the KCl matrix, a point that is discussed below. Secondly, the retention times of the two peaks are only marginally affected, and it is only the peak for Mg(II) which shows a significant loss in efficiency. It would appear that as chelation is playing a greater role in the retention of Ca(II) than in the retention of Mg(II), it is Ca(II) which is less affected by sample

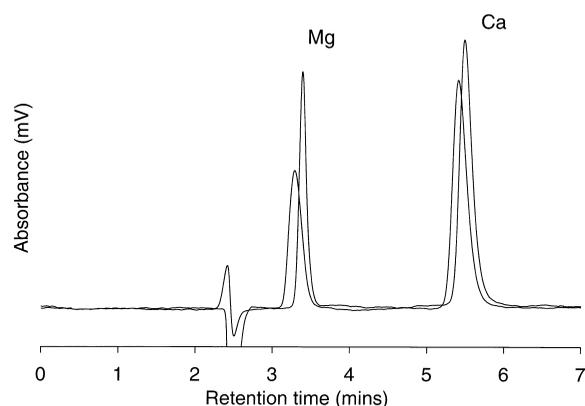


Fig. 6. Overlaid chromatograms showing the separation of 1 mg/l Mg(II) and Ca(II) standards prepared in water and in 1.0 M KCl on an IDA-silica column with a 1.0 M KNO₃ eluent, adjusted to pH 4.9 using HNO₃.

ionic strength, despite the fact that here the ionic strength of the sample matches that of the eluent.

Two other chloride salt matrices were also investigated, namely NaCl and LiCl. The separation of 1 mg/l Mg(II) and Ca(II) in 1.0 M solutions of the above two salts is shown in Fig. 7A and B (eluent conditions as in Fig. 6). In both cases there was a detector disturbance due to the matrix eluting at the eluent dip. In the case of 1.0 M LiCl the disturbance

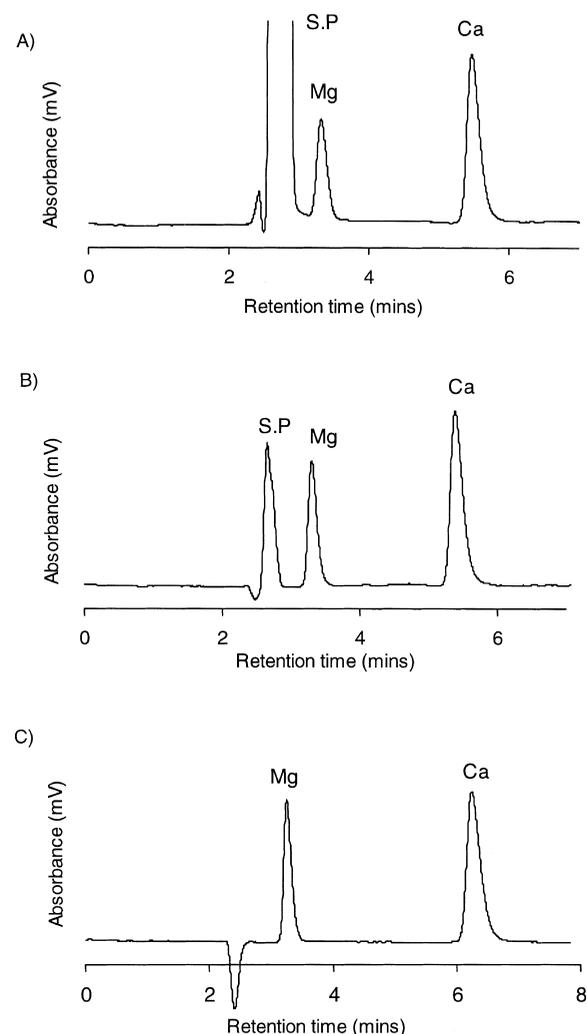


Fig. 7. Chromatograms showing the separation on an IDA-silica column of 1 mg/l Mg(II) and Ca(II) in (A) 1.0 M LiCl, (B) 1.0 M NaCl, with a 1.0 M KNO₃ eluent (pH 4.9) and (C) the separation of 1 mg/l Mg(II) and Ca(II) in 1.0 M NaCl with a 1.0 M NaNO₃ eluent (pH 4.9). S.P.=System peak.

was quite significant. This was due to the fact Li behaves differently to other alkali metals, namely K and Na, in that it is known to form very weak complexes with certain metallochromic ligands, including *o*-CPC [25]. As no such system disturbance was observed when analysing a KCl containing sample using a KNO₃ eluent, the disturbance from the NaCl containing sample was assumed to be due to the Na cation. To eliminate these system disturbances it was clear the eluent cation had to match that of the sample. To illustrate this, Fig. 7C shows the separation of 1 mg/l Mg(II) and Ca(II) in 1.0 M NaCl using a 1.0 M NaNO₃ eluent. As can be seen from Fig. 7C, by matching the eluent cation with that of the sample, the system peak can be eliminated completely. Using either a KNO₃ or NaNO₃ eluent has little effect upon selectivity for the two metal ions, except for the slightly increased retention of Ca(II) with the NaNO₃ eluent. Increasing the ionic strength of the sample further led to the reappearance of these system peaks, although it was possible, using a 1.0 M NaNO₃ eluent, to inject samples containing up to 3.0 M NaCl without the system peak interfering with the peaks for Mg(II) and Ca(II).

3.5. Analytical performance data

Before applying the developed method to the analysis of real samples the usual analytical performance criteria were investigated. Table 1 shows

the results obtained for linearity over high and low analyte concentration ranges, detection limits in water and 1.0 M NaCl, and peak reproducibility. The above parameters were determined under an analytical routine whereby at the end of each day the analytical column was flushed through with ~50 ml of a 0.1% HNO₃ solution, to remove any build-up on the column of transition metals or trivalent metal ions originating from the eluent/sample. The build-up of these highly retained metals would otherwise eventually (over a period of several days) lead to a reduction in column capacity and thus reduce retention times and separation efficiency.

From Table 1 it can be seen that the post-column reaction with *o*-CPC is particularly sensitive to Ca(II) and Mg(II). This is due to the uncomplexed ligand being almost colourless at pH 10.0 (thus producing relatively little background noise), but forming a dark purple coloured complex with the above two metal ions [26]. However, *o*-CPC is not particularly sensitive to Ba(II) and Sr(II). Therefore, if trace determinations of these two alkaline earth metals are required, an alternative ligand such as sulfonazo III may be preferable, this being one of the most sensitive metallochromic ligands available for the determination of Ba(II) [26].

3.6. Analysis of NaCl and KCl brine solutions

The developed method was applied to the determination of Mg(II) and Ca(II) in a 0.9% NaCl

Table 1
Analytical performance data

	Mg(II)	Ca(II)	Sr(II)	Ba(II)
<i>Linearity</i> (<i>n</i> =6)				
0.1–1.0 mg/l	$R^2=0.999$	$R^2=0.999$	–	–
1.0–10.0 mg/l	$R^2=0.999$	$R^2=0.999$	–	–
<i>Absolute detection limits</i> (ng) ^a				
In water	0.8 (±0.1)	0.7 (±0.1)	4.8 (±0.5)	29.0 (±3.0)
In 1.0 M NaCl	1.6 (±0.2)	1.4 (±0.2)	–	–
<i>Reproducibility</i> (RSD, %) (<i>n</i> =11) ^b				
Retention time	0.7	1.0	–	–
Peak height	2.5	1.4	–	–
Peak area	0.3	0.3	–	–

^a Calculated as twice the peak to peak baseline noise, 100 µl injection volume.

^b Based on 1.0 mg/l standards.

medical eyewash saline solution using standard addition over the range 0.1 to 1 mg/l ($n=4$). Under the conditions used in Fig. 7C, namely a 1.0 M NaNO₃ eluent, the saline sample was found to contain 180 µg/l Ca(II), with the Mg(II) concentration below the detection limit (16 µg/l). Overlaid chromatograms of the saline solution itself (a) and (b) the same sample spiked with 200 µg/l Mg(II) and Ca(II) are shown as Fig. 8A. The chromatograms show how trace amounts of Ca(II) were easily detectable in an approximately 20 000-fold excess concentration of Na through using the correct choice of eluent, without any large matrix peaks or significant affect upon selectivity or peak efficiency.

The method was also applied to the determination of Mg(II) and Ca(II) in a 0.5 M solution of laboratory-grade KCl (Fluka >99%), this time using a 1.0 M KNO₃ eluent. Once again standard addition was used and the sample was found to contain a Mg(II) concentration of 210 µg/l Mg and a Ca(II) con-

centration which fell below the method detection limit (14 µg/l). The overlaid chromatograms of the (a) 0.5 M KCl sample and (b) the same sample spiked with 300 µg/l Mg(II) and Ca(II) are shown as Fig. 8B. As above, through the correct choice of eluent conditions, no matrix peak was observed and Mg(II) and Ca(II) both elute as sharp well resolved peaks in under 6 min (although not the case with the above two samples, when analysing real samples which contain increased concentrations of acidic or basic components it may be necessary to buffer the eluent with a suitable non-complexing buffer to reduce changes in retention times due to high or low sample pH).

4. Conclusion

The ion chromatographic separation of alkaline earth metals has been investigated using an IDA bonded silica column. Results clearly indicate a mixed mode retention mechanism over the range of eluent conditions investigated with the dominance of ion exchange or chelation being dependent upon eluent ionic strength and pH. The correct choice of eluent allows the efficient and well resolved separation of alkaline earth metal ions in samples of significant ionic strength without large matrix peaks or signs of “self elution”. Trace concentrations of Mg(II) and Ca(II) at the low µg/l level could be easily detected in NaCl and KCl brine samples by using sensitive post-column reaction detection with *o*-cresolphthalein complexone.

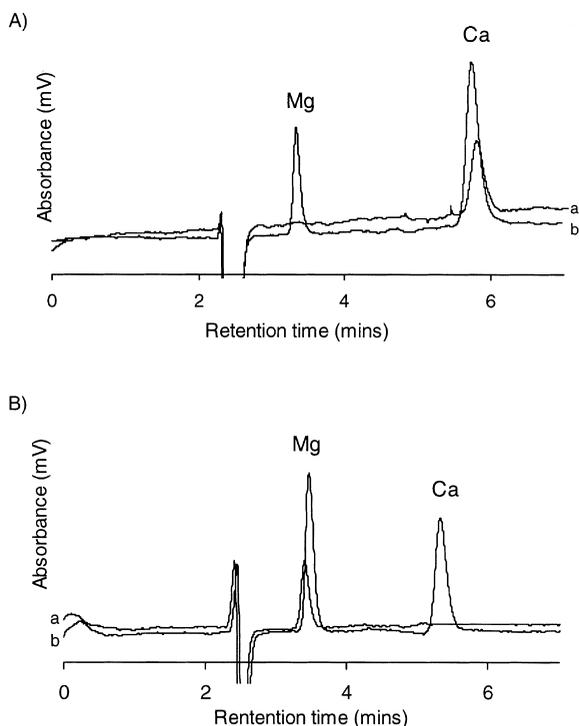


Fig. 8. Chromatograms showing (A) saline eyewash sample (0.9% NaCl) overlaid with spiked (200 µg/l) sample and (B) 0.5 M KCl sample solution overlaid with spiked (300 µg/l) sample. Other conditions: (A) as in Fig. 7C, (B) as in Fig. 6.

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