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Determination of calcium and magnesium in water samples by high-performance liquid chromatography on a graphitic stationary phase with a mobile phase containing *o*-cresolphthalein complexone

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Abstract

A sensitive and selective liquid chromatographic procedure for the separation and visible detection of alkaline earth metals in complex saline matrices has been developed. A mobile phase containing the selective metallochromic chelating ligand, *o*-cresolphthalein complexone, was used to dynamically coat a pH tolerant reversed-phase porous graphitic carbon column. A dynamic chelating ion-exchange mechanism facilitated the separation of alkaline earth metals, which were detected using a spectrophotometric detector at 575 nm. Detection limits of 0.05 mg l^{-1} for magnesium and 0.10 mg l^{-1} for calcium were obtained in samples containing in excess of 2300 mg l^{-1} of sodium, without interference. The procedure was applied to the determination of magnesium and calcium in a range of environmental waters, including saturated saline Antarctic lake samples, with the results comparing well to those achieved using capillary electrophoresis, atomic absorption spectroscopy, inductively coupled plasma mass spectrometry and standard complexometric titration methods. © 1997 Elsevier Science B.V.

Keywords: Water analysis; Mobile phase composition; Calcium; Magnesium; Alkaline earth metals; Cresolphthalein complexone; Metal cations

1. Introduction

The determination of alkaline earth metals, particularly calcium and magnesium, is of importance in environmental, biological and industrial applications. Ion chromatography (IC) combined with conductimetric detection enables the separation and detection of sub mg l^{-1} levels of alkaline earth ions [1,2]. However, when analysing complex sample types, for example those with high ionic strengths or a very high ratio of alkali to alkaline earth metals, IC, especially when used in isocratic mode, suffers such problems as large matrix peaks and baseline disturbances, which are predominantly related to the universal nature of the conductivity detector.

An alternative to conductiometric detection in IC is the use of post-column reaction (PCR) combined with spectrophotometric detection. This has been applied mainly to the detection of transition and rare earth metals ions using metallochromic ligands such as 4-(2-pyridylazo)resorcinol (PAR) [3–5] and arsenazo III [6–8] as PCR reagents. Ligand-exchange reagents such as PAR/ZnEDTA [9,10] have been developed for the PCR detection of alkaline earth metal ions and this approach offers the advantages of both sensitivity and selectivity. However, the use of PCR detection requires the addition of one or more reagent delivery systems to the conventional high-performance liquid chromatography (HPLC) instru-

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mentation in order to deliver the PCR reagent, as well as the use of long reaction coils to facilitate adequate mixing of the eluent and PCR reagent. Inclusion of a colour-forming metallochromic ligand into the eluent provides a way of simplifying the above systems by removing the need for the instrumentation necessary for PCR reagent addition. This approach has been applied in IC by Zenki [11] and Toei [12–17] using chlorosulfonazo III [11], *o*-cresolphthalein complexone [12–14], arsenazo III [15,16] and xylenol orange [17] as the metallochromic ligand. In most of the above examples, the metal ions were retained by a conventional ion-exchange mechanism and coloured metal complexes were formed, enabling direct visible spectrophotometry, at the appropriate wavelengths, to be used for detection.

o-Cresolphthalein complexone (OCPC) is one of the most sensitive metallochromic ligands available for the determination of alkaline earth metal ions. Toei [12–14] used OCPC as a component of an ion-exchange eluent and applied the system to the separation and detection of alkaline earth metals. Calcium and magnesium were determined in a range of complex sample types, including seawater. In these systems the optimum eluent pH for the separation was found to be between 3 and 6, at which pH OCPC does not complex alkaline earth metals, so the post-column addition of an ammonium buffer was required to raise the pH to 10.2, where the metal complexes are sufficiently stable to be detected spectrophotometrically at 572 nm.

In a recent preliminary communication [18], a liquid chromatographic technique was reported for the separation and detection of calcium and magnesium, in which OCPC was used as a component of the mobile phase employed with a pH tolerant porous graphitic carbon reversed-phase column. The use of this column allowed the mobile phase pH to be increased to 10.5, thereby removing the requirement for addition of any post-column buffering reagents. The OCPC added to the mobile phase acted to dynamically coat the stationary phase with the ligand and to establish a dynamic chelating ion-exchange mechanism for the retention of calcium and magnesium. The analytes were eluted as coloured complexes and were detected using a spectrophotometric detector at 572 nm. The separation of calcium and magnesium was achieved in under 10 min, although peak shapes were relatively poor and in real samples the peaks were not totally resolved. This type of chelating ion-exchange mechanism has also been applied to the separation of alkaline earth and transition metals using polymeric resins pre-coated with OCPC, although in these cases the ligand itself was not included as a component of the mobile phase [19–21].

In the present paper a more detailed investigation into the above method is described. Improvements in both peak shapes and resolution of calcium and magnesium have been achieved, allowing the complete resolution of calcium, magnesium and strontium in under 12 min. The method detection limits have also been reduced substantially, with sub mg l^{-1} concentrations of both calcium and magnesium being easily detectable in samples containing very large excesses of sodium. The improved method has been applied to the determination of calcium and magnesium in a range of real samples of varying salinity, with the results comparing well to a number of alternative analytical techniques.

2. Experimental

2.1. Instrumentation

A Waters (Milford, MA, USA) Model 600 programmable pump was used to deliver the mobile phase. Sample injection was via a Rheodyne (Cotati, CA, USA) Model 7125 syringe loading injector, fitted with either a 5, 20 or 100 μl sample loop. The analytical column used was a Hypercarb porous graphitic carbon reversed-phase column (100×4.6 mm I.D.), combined with a guard column (10×4.6 mm I.D.), supplied by Shandon HPLC (Runcorn, UK). A Waters Model 481 UV–Vis spectrophotometric detector interfaced to a Waters Maxima 820 data station was used to monitor the eluting complexes at 575 nm.

A Varian SpectrAA 800 Atomic Absorption Spectrophotometer (Varian, Melbourne, Australia), a Finnigan Element inductively coupled plasma mass spectrometer (Bremen, Germany) and a Waters Quanta 4000 capillary electrophoresis system were used to provide comparative results for the samples

analysed and were operated in accordance with manufacturers recommendations [27,28]. A Shimadzu (Tokyo 101, Japan) UV160 UV–Vis recording spectrophotometer was used to record the spectra of the mobile phase and complexed alkaline earth metals.

2.2. Reagents

OCPC (3,3′-bis[N,N-bis(carboxymethyl)aminomethyl]-*o*-cresolphthalein), 99% dye content, was obtained from Fluka (Buchs, Switzerland) and was used without further purification. Methanol (HPLC grade) was supplied by Ajax Chemicals (Sydney, Australia). All other chemicals were obtained from BDH (Kilsyth, Australia) and were of analytical-reagent grade unless stated otherwise. Solutions were prepared using distilled and deionised water from a Millipore (Bedford, MA, USA) Milli-Q water purification system. Mobile phases were prepared by dissolving the desired amounts of OCPC and other components in aqueous methanol and then buffered to pH 10.0 using 20 m*M* boric acid (this buffer concentration was kept constant throughout the study). The mobile phase was then filtered using a 0.45 μm disc filter and degassed using an ultrasonic bath prior to use. Once prepared, the mobile phase remained stable for several days if stored away from direct sunlight. Standard solutions of metal ions were prepared in 0.1 *M* HNO_3 using nitrate and carbonate salts and were diluted as required. Samples were analysed untreated, except for dilution where necessary.

3. Results and discussion

3.1. o-Cresolphthalein complexone

OCPC is a triphenylmethane based chelating ligand containing two iminodiacetic acid functional groups. It complexes with a number of polyvalent metals but only forms characteristic deep purple coloured complexes (MHL^{3-}) with the alkaline earth metals. It is readily soluble in aqueous alkaline solutions and common organic solvents. At pH 10.0–11.0 a solution of the ligand is slightly pink in colour ($pK_{a4}=7.8$, $pK_{a5}=11.4$), predominately due to impurities such as *o*-cresolphthalein, which is one of the starting materials used in the synthesis of the reagent [22]. However, with the addition of 30% or more of an organic solvent, such as methanol, this colour is almost totally suppressed. Fig. 1 shows the absorbance spectrum of a typical mobile phase used in this study, consisting of 0.4 m*M* OCPC, 60% (v/v) methanol, 20 m*M* boric acid and 50 m*M* sodium chloride at pH 10.0. Also shown are the absorbance spectra after 5 mg l^{-1} calcium and magnesium had been added to the mobile phase. Under the above conditions the calcium complex gave a molar absorptivity of $4.6\cdot10^3$ l mol^{-1} cm^{-1} at 575 nm, which is considerable less than the literature value [23]. However, the background absorbance of the mobile phase itself at 575 nm was found to be very low, suggesting that sensitive direct detection should be possible.

3.2. Retention mechanism

At pH 10.0 OCPC (H_6L) exists as H_2L^{4-} and in the presence of alkaline earth metal ions, MHL^{3-} complexes are formed [22]. When using the graphitic carbon reversed-phase column with a 60% methanol mobile phase adjusted to pH 10.0, injection of the OCPC ligand gave a peak close to the solvent front. The retention of the OCPC peak could be increased substantially with a reduction in the percentage of methanol in the mobile phase, suggesting typical reversed-phase adsorption behaviour on the stationary phase. By including the uncomplexed ligand in

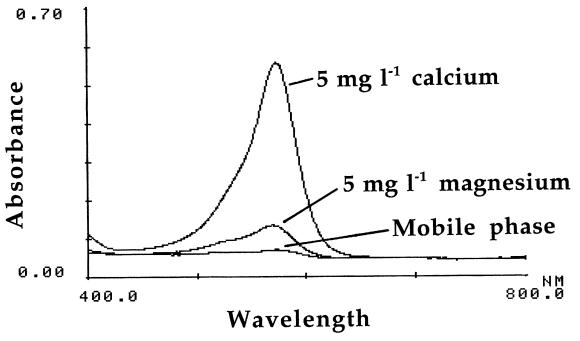

Fig. 1. Absorbance spectra of a typical mobile phase and the same mobile phase containing 5 mg l^{-1} of calcium or magnesium. Conditions: 60% methanol, 20 m*M* boric acid, 50 m*M* NaCl and 0.4 m*M* OCPC at pH 10.0.

the mobile phase the system becomes analogous to reversed-phase ion-interaction chromatography. Here, it is proposed that the ligand establishes a dynamic equilibrium between the mobile and stationary phases, becoming adsorbed onto the surface of the stationary phase and thereby producing a surface layer which can participate both in ion exchange and in chelation of the analytes. The total concentration of the ligand adsorbed onto the stationary phase at any time is controlled by the percentage of organic solvent in the mobile phase. When alkaline earth metal ions are introduced into the system they travel through the column in equilibrium with the ligand in the mobile phase and the ligand on the stationary phase. Retention can be considered to be caused by a dynamic chelating ion-exchange mechanism in which mobile phase complexation, stationary phase complexation, and ion-exchange interaction with the adsorbed OCPC anions can all contribute to retention. The metal ions are eluted in the form of their coloured OCPC complexes and can be detected using a spectrophotometric detector at 575 nm.

Retention of the alkaline earth metal ions can be controlled through the concentration of organic modifier in the mobile phase since this effectively alters the dynamic capacity of the stationary phase by reducing the concentration of adsorbed ligand. Fig. 2 shows the relationship between the logarithm of the concentration of methanol added to the mobile phase and the capacity factors of calcium and magnesium. The results illustrate that the addition of methanol gives reduced stationary phase capacity and increased OCPC in the mobile phase, both of which lead to a decrease in retention.

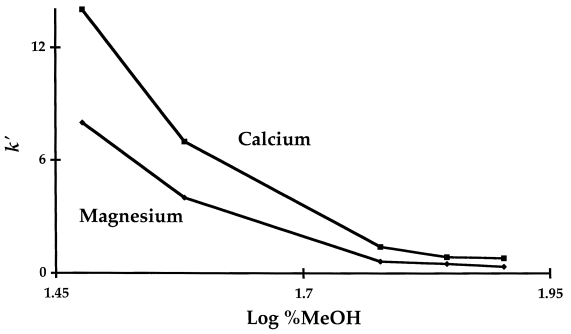

Fig. 2. Effect of methanol concentration on the capacity factor of calcium and magnesium. Conditions: 20 m*M* boric acid and 0.4 m*M* OCPC at pH 10.0. Flow-rate 1 ml min^{-1}.

The elution order of the alkaline earth ions gives some insight into the retention mechanism that is operating. Ion-exchange selectivities dictate that the elution order should be magnesium, calcium, strontium, barium (A), if retention was solely by ion-exchange. On the other hand, in a situation where the chelating ligand was present only in the stationary phase, and chelating ion-exchange were the sole retention mechanism, the metal ions should be eluted in order of decreasing conditional formation constants [24], so that the expected order would be barium, strontium, calcium, magnesium (B). This expectation has been shown to be correct in previous studies [20,21]. When using polymeric reversed-phase columns, pre-coated with OCPC, combined with eluents which did not contain OCPC, the elution order obtained for the alkaline earth metals was indeed barium, strontium, calcium, magnesium. In the above work high ionic strength eluents, such as 1 *M* KNO_3, were used to suppress any retention due to ion-exchange and assure that the elution order seen was solely due to chelation ion-exchange.

However, the mechanisms involved in retention become less predictable when the ligand is present in both the stationary and mobile phases, as is the case here. Now the final elution order will be dependent on the relative concentrations of the ligand in the two phases. A preponderance of adsorbed ligand should give the elution order shown in (B) above. Of course, mixed retention mechanisms leading to unpredictable elution orders are also possible.

3.3. Optimisation of the mobile phase composition

In the development of a chromatographic method such as this the variables to be considered in the optimisation of the mobile phase composition are ligand concentration, concentration of organic modifier, mobile phase ionic strength, mobile phase pH and the concentration of any additional complexing agents.

In preliminary studies [18], variation of the methanol concentration (50–80%) and ligand concentration (0.2–0.8 m*M*) in the mobile phase showed that calcium and magnesium could be separated within 10 min with an R_s value of about 1.0, using a mobile

phase consisting of 58% methanol and 0.4 m*M* OCPC, but exhibiting only moderate efficiency. The resolution of calcium and magnesium was found to be slightly improved with a reduction in the percentage methanol, although this led to longer run times and broader peaks. The appearance of these broad peak shapes when using chelating ion-exchange has been attributed in similar chromatographic systems to slow chelation-exchange kinetics [18–21]. Increasing the mobile phase concentration of OCPC (up to 0.8 m*M*) led to a decrease in the retention of both calcium and magnesium, as this effectively increased the degree of mobile phase complexation. Peak resolution was found to be the greatest between 0.2–0.4 m*M* OCPC.

In an attempt to improve on the above separation the effects of the remaining mobile phase parameters were studied. Firstly, the effect of adding a competing complexing agent to the mobile phase was investigated. Citrate was selected as a moderately strong complexing agent for the alkaline earth metal ions and 0.1–0.6 m*M* citrate was shown to reduce the intensity of colour of a 0.4 m*M* OCPC solution containing 5 mg l^{-1} calcium. At the highest concentration of citrate the solution was decolourised completely. Adding citrate to the mobile phase in the concentration range 0–0.3 m*M* did not produce any significant improvements in peak shapes, although as expected a decrease in capacity factors for calcium, and to a lesser extent magnesium, was noticed. This behaviour is illustrated in Fig. 3. It should also be noted that the addition of citrate to the mobile phase resulted in a significant reduction in peak areas due to the high stabilities of the citrate complexes compared to the OCPC complexes [25]. It was concluded that including an additional complexing agent did not significantly improve peak shapes and so was not further investigated.

In previous work by Jones et al. [26] with similar iminodiacetic acid metallochromic ligands coated dynamically on polymeric resins, it was found that the influence on retention exerted by cation-exchange could be manipulated by increasing the ionic strength of the mobile phase. Therefore, the effect of adding NaCl to the mobile phase was investigated in the present system and the results are presented in Fig. 4. As can be seen in the figure the retention times of each metal ion increased with the addition of NaCl. Fig. 4 suggests that the dynamic capacity of the stationary phase has been increased as a result of salting-out effects and that this effect has overshadowed any decreased retention which might be due to ion-exchange competition from the added sodium ions. It is also noteworthy that the inclusion of between 0.1 and 0.2 *M* NaCl in the mobile phase led to a substantial improvement in peak shapes and the resolution of calcium and magnesium. Fig. 5 shows the separation of magnesium and calcium obtained with the addition of 0.2 *M* NaCl to the mobile phase. These conditions also allowed strontium to be separated from calcium, but the strontium peak was severely tailed and sensitivity was approximately ten times less than for calcium and magnesium. This is due to the low stability of the

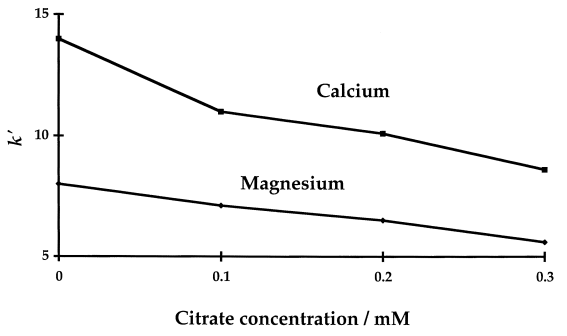

Fig. 3. Effect of citrate added to the mobile phase on the capacity factors of calcium and magnesium. Conditions: 40% methanol, other conditions as for Fig. 1. Flow-rate 1 ml min^{-1}.

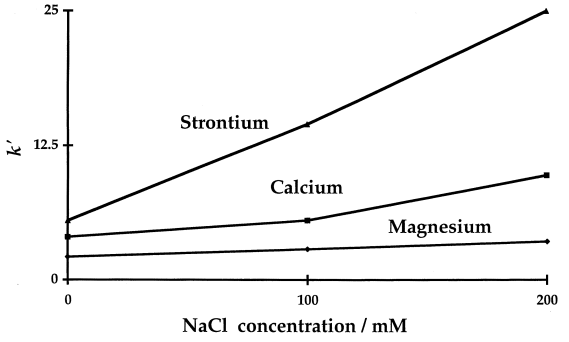

Fig. 4. Effect of NaCl added to the mobile phase on the capacity factors of calcium and magnesium. Conditions: 55% methanol, other conditions as for Fig. 1. Flow-rate 1 ml min^{-1}.

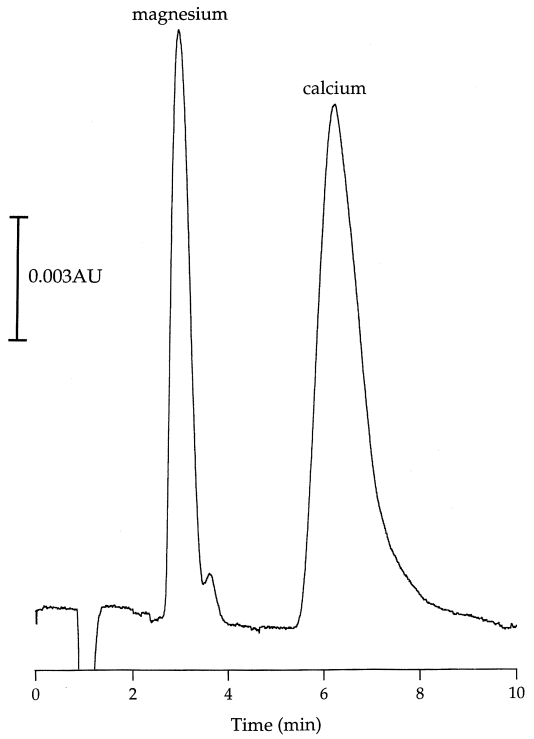

Fig. 5. Chromatogram showing the separation of calcium and magnesium. Conditions: 25 mg l^{-1} mixed metal standard, 5 μl injection volume. Mobile phase: 55% methanol, 20 m*M* boric acid, 0.2 *M* NaCl and 0.4 m*M* OCPC at pH 10.0. Flow-rate 1.4 ml min^{-1}.

strontium complex at pH 10. No peak for barium could be obtained under these conditions for the same reason. The retention order achieved was magnesium, calcium then strontium.

The effect of the mobile phase pH was investigated in the range 9.1–10.0 and it was found that the retention times of both magnesium and calcium varied only slightly over this range. This is due to the fact that OCPC is present in both the stationary and mobile phases, so a change in pH should not lead to a change in the distribution coefficient of the metal ions. However, the detector response for both metal ions, especially calcium, increased at higher pH values, as shown in Fig. 6. This effect can be attributed to higher conditional formation constants leading to increased levels of complexation of the metal ions. Therefore, pH 10.0 was used for all further studies. A further increase in pH led to a substantial increase in background absorbance.

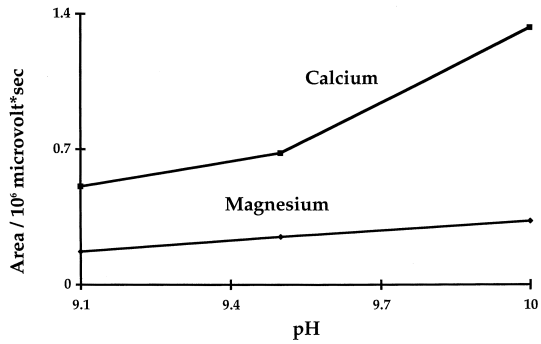

Fig. 6. Effect of the mobile phase pH on detector response for calcium and magnesium. Conditions: as in Fig. 5.

We turn now to an evaluation of the above results in terms of the probable retention mechanism(s). The elution order is consistent with either an ion-exchange mechanism or a chelation mechanism in which the major complexation effects are exerted by the mobile phase. The effect of added NaCl in Fig. 4 does not support the hypothesis that retention is strongly dependent on ion-exchange. Inconsistency of the observed elution order with that obtained by Toei [14] for a bonded iminodiacetic acid column also suggests that ion-exchange plays a less significant role in the present system. Finally, the observed elution order differed to that for OCPC-coated polymeric stationary phases used with mobile phases which did not contain the ligand [20,21], which again suggests a predominance of mobile phase chelation. It is therefore not possible to predict the elution order based on conditional formation constant data alone, since retention is dependent upon the relative concentrations of the ligand in the stationary and mobile phases. To determine if this was indeed the case, a 0.05 *M* NaCl mobile phase at pH 8.6 was prepared without either methanol or OCPC and this was used with a column which had been previously coated with OCPC. Strontium was eluted before calcium and magnesium, which corresponds to the above work using pre-coated polymeric columns. This elution order confirmed that it is the relative concentrations of the ligand in the mobile and stationary phase which controls the elution order of the alkaline earth metals. This is also supported by results presented earlier [18], where the retention times of calcium and magnesium were shown to

increase with a reduction in the concentration of the ligand added to the mobile phase.

3.4. Analytical performance characteristics

The linearity of the system for calcium and magnesium was determined using standards prepared both in deionised water and 0.5 *M* NaCl. Calibration plots based on peak area showed a distinctive upward curvature when the standard concentration range covered two or more orders of magnitude, but over narrower concentration ranges this effect was no longer apparent. For example, with a 100 μl injection volume and standards containing 0–20 mg l^{-1}, correlation coefficients of $R^2=0.996$ and $R^2=0.998$ were obtained for magnesium and calcium, respectively. Peak heights were found to give best linearity because of the difficulty in accurately determining peak areas for the relatively broad peaks obtained with this chromatographic system.

Detection limits determined at three times the standard deviation of the background signal were 0.05 mg l^{-1} for magnesium and 0.10 mg l^{-1} calcium using samples containing 0.1 *M* NaCl (23 000-fold excess). The sensitivity of the method is evident from Fig. 7 which shows the chromatogram obtained for a standard containing 1 mg l^{-1} of calcium and magnesium and 2300 mg l^{-1} of sodium. A signal at the solvent front is caused by the sodium but this is totally resolved from the adjacent magnesium peak. Improvement of the resolution between magnesium and sodium was achieved by adding 0.2 *M* NaCl to the mobile phase and reduction of the methanol content to 45%.

Precision was determined for repeat injections of standards prepared in both deionised water and in 0.1 *M* NaCl. Replicate 5 μl injections ($n=8$) of a 100 mg l^{-1} mixed calcium and magnesium standard prepared in deionised water gave R.S.D. values of 5.6 and 4.0% for peak height, 4.2 and 7.2% for peak area, and 4.4 and 1.7% for retention time, respectively. Replicate 20 μl injections ($n=5$) of a 50 mg l^{-1} mixed metal ion standard, prepared in 0.1 *M* NaCl, gave R.S.D. values of 4.2 and 5.7% for peak height, 5.6 and 4.1% for peak area, and 2.8 and 4.0% for retention time, for calcium and magnesium, respectively.

Possible interferences were investigated using 20 μl injections of mixed 5 mg l^{-1} calcium and magnesium standards containing a 50-fold excess of potassium, barium and strontium. No significant effects on peak area or retention time were observed at these levels. Potential interferences from transition metals were not investigated due to solubility problems at pH 10 and because previous studies carried out by Toei [14] when using a bonded chelating ion-exchange column with a OCPC mobile phase showed no interferences from iron(III), cobalt(II), copper(II), zinc(II), nickel(II) and aluminium(III), at concentrations five-times greater than that of calcium and magnesium.

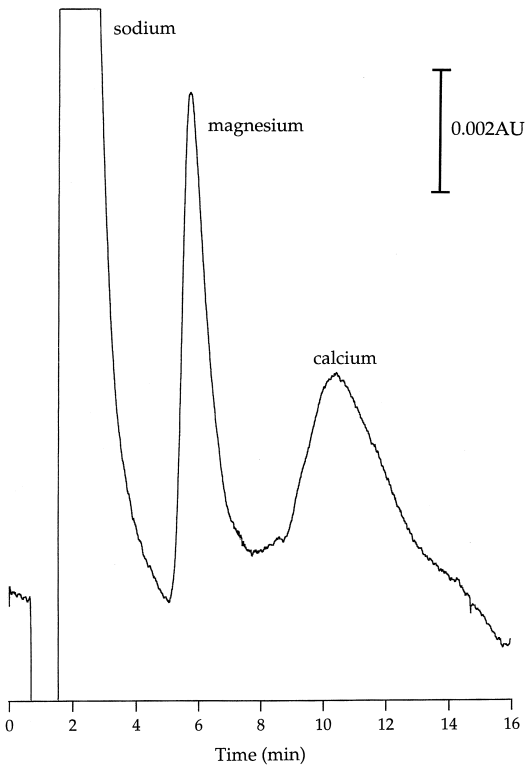

Fig. 7. Chromatogram showing the separation of calcium and magnesium in a standard containing excess sodium chloride. Conditions: 1 mg l^{-1} calcium and magnesium, 2300 mg l^{-1} sodium, 100 μl injection volume. Mobile phase: 45% methanol, other conditions as for Fig. 5. Flow-rate 1 ml min^{-1}.

3.5. Analysis of water samples

Three types of water samples exhibiting a range of calcium and magnesium concentrations were ana-

Table 1
Comparative analyses of water samples using the proposed HPLC method, atomic absorption spectroscopy (AAS), capillary zone electrophoresis (CZE), complexometric titration (CT) and inductively coupled plasma mass spectrometry (ICP-MS)

Water sample	Analyte	HPLC	AAS	CZE[3]	CT	ICP-MS[4]
NATA	Mg	92 (5)	89.3	88.4	–	–
N065[1]	Ca	115 (6)	104.5	108.3	–	–
Mine Process Water[1]	Na	–	–	–	–	330
	Mg	161 (9)	–	161	–	190
	Ca	286 (14)	–	211	–	250
Deep Lake (surface)[2]	Na	–	–	–	60.7	–
	Mg	13.34 (0.76)	–	–	13.38	–
	Ca	2.11 (0.08)	–	–	2.19	–
Deep Lake (20 m depth)[2]	Na	–	–	–	61.0	–
	Mg	13.23 (0.74)	–	–	13.93	–
	Ca	1.82 (0.09)	–	–	2.21	–
Deep Lake (25 m depth)[2]	Na	–	–	–	61.3	–
	Mg	13.08 (0.73)	–	–	13.96	–
	Ca	1.94 (0.10)	–	–	2.21	–

[1] Values in mg l^{-1} ($\pm$S.D.).
[2] Values in g l^{-1} ($\pm$S.D.).
[3] Samples diluted 200 times.
[4] Samples diluted 500 times.

lysed using the developed technique and the results are given in Table 1. The samples chosen varied considerably in sodium content, ranging from a freshwater standard reference sample (NATA N065) to saturated brines taken from various depths in Deep Lake, Antarctica. The NATA and mine process samples were analysed directly by the HPLC method, whereas the Antarctic lake samples were diluted twenty times with deionised water. Table 1 compares the results obtained from the HPLC method with those obtained using a number of alternative methods. Good agreement was observed in the majority of cases.

4. Conclusions

A sensitive and selective liquid chromatographic procedure for the determination of calcium and magnesium in complex matrices has been developed. The method employed a colour forming metallochromic ligand as a component of the mobile phase, used in conjunction with a graphitic carbon reversed-phase analytical column, and permitted the determination of calcium and magnesium at sub mg l^{-1} concentrations in samples containing large excesses of alkali metal ions. Retention was proposed to be due to a dynamic chelating ion-exchange mechanism with the relative concentrations of the chelating ligand in the stationary and mobile phases governing the elution order achieved. The method was shown to be reproducible, linear and relatively free of interferences. The results obtained for a variety of water samples compared well to those from a number of alternative instrumental analytical techniques.

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