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Ethylenediamine as eluent component in cation chromatography. Predictive and comparative study for analysis of alkaline earth ions

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Abstract

The retention behaviour of alkaline earth cations was studied as a function of changing composition of acidified ethylenediamine eluent. The multiple eluent species retention model developed for separation of calcium, magnesium and strontium ions was utilized for determination of selectivity coefficients for sample and eluent ions. The suggested model accurately describes and predicts retention of analytes under elution conditions [0.5–2.0 mM C₂H₄(NH₂)₂ and pH 4–6] which are of practical importance. The results in three-dimensional retention surface with species distribution graphs are demonstrated. Complexometric titrations and ion chromatography (IC) were compared for the analysis of calcium and magnesium ions. Statistical data indicated that there was no evidence for relative differences between the two methods. However, IC gives several advantages over volumetric method. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Mobile phase composition; Retention models; Ethylenediamine; Alkaline earth ions

1. Introduction

Divalent metals are more strongly retained by cation exchangers and require an eluent containing a divalent cation in the acidic pH range. In separation systems which involve purely ion-exchange mechanisms, alkaline earth cations are eluted with ethylenediamine ions, C₂H₄(NH₃)₂²⁺, (EnH₂²⁺) using nonsuppressed conductivity detection [1]. Therefore, an eluent containing a protonated divalent amine is much more powerful eluent than only a hydrogen ion. In addition, a dilute acidic concentration can be used for elution. This results in lower background conductivity in detection. Molar conductivity of the eluent is lower than that of alkaline-earth metals,

therefore the conductivity rises as the cations elute. Thus, conductometric detection is a logical choice for these nonchromophoric ions. Other possible eluents are the protonated cations of aromatic amines using direct conductivity detection [2]. Because most of these are highly toxic, they are usually not used. In many other cases however complexing agents (tartarate, oxalate and hydroxybutyrate) are also added to the ethylenediamonium eluents in order to accelerate the elution of transition or rare earth metals or to manipulate the selectivity which can be attained by ion-exchange alone [3]. In suppressor based ion chromatography (IC), a gradient system has been shown to be useful for cation separation with diaminopropionic acid eluent [4]. In isocratic operation, a micromembrane suppressor combined with dipolar histidine as eluent is now used for the separation of alkali and alkaline-earth metals [5]. A

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polybutadiene–maleic acid coated silica cation exchanger was developed for the isocratic separation of cations [6]. The separation was accomplished using organic acid eluents containing complexing components. Other approaches use inorganic eluents as copper sulfate [7] along with indirect UV detection and acidified zinc-nitrate with suppressed conductivity monitoring [8]. The main advantage of nonsuppressed cation chromatography on a sulfonic acid cation-exchange column along with ethylenediamine eluent for routine analyses is that the instrumentation is simpler, since no suppressor is required. The analytical separation process is quite easy to set up and use. The system has further advantages compared to the other technique including: shorter run times, simple isocratic operation, manipulation of elution power by the pH, no system peak interference in retention interval of analytical peaks and lower operational cost. Particular emphasis has been placed on IC separation of alkali, alkaline-earth metals and ammonium as well as organic amine cations because these ions are found in many types of samples.

The primary retention mechanism in cation chromatography is the electrostatic interaction and competition between the analyte cation and eluent ion for the charged strongly acidic functional group in the stationary phase. However, the fact that there are secondary chemical equilibria in the retention mechanism in addition to primary retention process is well known [9]. In our previous paper retention equations were derived and examined in the suppressed IC separation of common divalent cations using dipolar histidine as eluent. This has become possible through the incorporation of secondary chemical equilibria such as protolysis of eluent components.

In this paper, retention equation is reported for divalent cations and it is demonstrated that the dependence of retention on pH and concentration of acidified ethylenediamine eluent can also be described by the multiple eluent species retention model. The ability of our retention model allows the analyst to predict the elution data in this separation system. A critical characterization of the model as a predictive tool for retention behaviour of alkaline earth cations is also presented. Further purposes of the present work are to provide quantitative data on

the selectivity of the IC system and comparative evaluation volumetric titration method in the determination of alkaline earth cations.

2. Theory

The retention theory is based on the extension of ion-exchange equilibrium by protonation of ethylenediamine. It will be a stoichiometric approach based on the mass action law. Retention models have been discussed in mathematical detail in our previous papers [9–11] and in Refs. [12,13]. This will not be repeated here. However, a short description of chemical equilibria of diprotic amine and the final form of retention equation will be presented. This is more complex because of the presence of protonation as the additional chemical equilibrium opportunity.

The ionization process of acidified ethylenediamine molecule can be abbreviated:



For the formation of eluent cations two protonation constants must be considered. These are $K_1 = 10^{9.93}$ and $K_2 = 10^{6.85}$ [14]. The mole fraction distribution diagram of ethylenediamine as a function of eluent pH is shown in Fig. 1. It has a similar appearance to the distribution diagram for diprotic acids. The monoprotonated form exists in appreciable concentration from pH 8 to pH 10. At pH values between 6 and 8 the eluent may exist as monovalent, divalent or mixture of both. The eluent takes up two protons in the wide acidic range (pH < 6.0). Therefore an eluent acidified with nitric acid should be

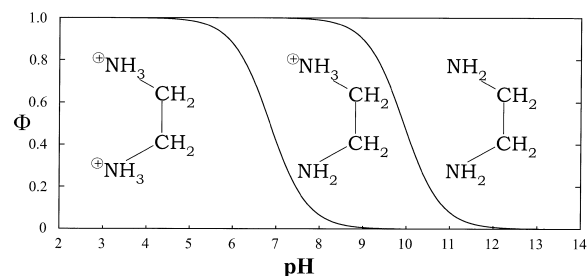
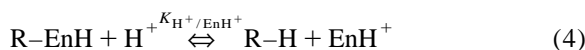
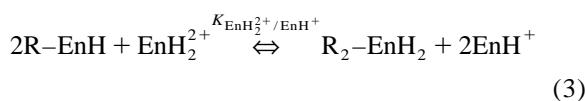
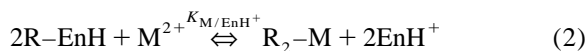


Fig. 1. The proton ionization equilibria of ethylenediamine eluent. Φ is the partial molar fractions of eluent species.

used for separation of alkali and alkaline-earth cations. As the mobile phase pH is changed simultaneous ion-exchange equilibria and protonation will take place between the stationary and mobile phases. At the eluent pH values used for separation three eluent components will be present (H^+ , EnH^+ and EnH_2^{2+}) with different elution power. The concentration of these ionic species in solution is dependent on the eluent pH. The retention of sample cations (M) and the interactions between the eluent species can be described by the following ion-exchange equilibria:



where R– denotes the cation-exchange stationary phase and K_{M/EnH^+} is the ion specific selectivity coefficient. Taking EnH^+ as the basis for eluent system two intereluent selectivity coefficients, $K_{EnH_2^{2+}/EnH^+}$ and K_{H^+/EnH^+} must be considered.

Developing the above equilibrium equations and determining the concentrations of eluent species in stationary phase lead to retention equation. The volumetric distribution coefficient, D_M of solute analyte, M^{2+} can be given in terms of selectivity coefficients of the system, ion-exchange capacity of the separation column, Q and the molar concentration of the eluent species:

$$D_M = \frac{v_0 k'}{v_{st}} = K_{M/EnH^+} \left(\frac{\sqrt{p^2 + q} - p}{4K_{EnH_2^{2+}/EnH^+} [EnH_2^{2+}]} \right)^2 \quad (5)$$

where

$$p = [EnH^+] + K_{H^+/EnH^+} [H^+],$$

$$q = 8K_{EnH_2^{2+}/EnH^+} Q [EnH_2^{2+}]$$

and v_0 is the void volume, v_{st} is the volume of the stationary phase. The molar concentrations of the three competing cations ($[EnH_2^{2+}]$, $[EnH^+]$, $[H^+]$) in

the eluent can be calculated from the analytical concentration of ethylenediamine (c_{En}) by the molar fraction of species (Φ) using protonation constants, K_1 and K_2 and the actual pH of the mobile phase, e.g., $[EnH_2^{2+}] = \Phi_2 c_{En}$, where $\Phi_2 = K_1 K_2 [H^+]^2 / (1 + K_1 [H^+] + K_1 K_2 [H^+]^2)$. Activities instead of concentrations were used in the actual data processing. The use of activities (a) is important in the case of EnH_2^{2+} , which has a greater impact on the cation separation ($a_{EnH_2^{2+}} = \gamma_2 \Phi_2 c_{En}$).

3. Experimental

3.1. Reagents and solutions

Eluents were prepared by using analytical-grade ethylenediamine (Fluka, Buchs, Switzerland). Ion-exchanged water was purified by a Milli-Q Plus System (Millipore, Bedford, MA, USA) containing a 0.45 μm filter at the outlet. Water for eluents was sparged with helium before use. The actual pH was monitored after the eluent was degassed, and the pH was controlled (Orion Model 420A, USA) by addition of diluted HNO_3 (Merck-Suprapur). The measurement of pH was carried out at 25 °C using an Orion Triode pH electrode, Model 9157BN with internal reference system. Standard sample solutions of cations were prepared by dissolution of chloride salts (Baker Analyzed Reagents, The Netherlands) with the exception of magnesium, which was prepared from sulfate. Stock solutions of the individual alkaline-metal cations were prepared with polypropylene volumetric apparatus.

3.2. Instrumentation

A Model Dionex-10 (Sunnyvale, CA, USA) chromatograph was used in this work. The major components of this system were a high-pressure pump, 100 μl loop, a cation separator column (100 \times 3 mm, BT IV KA, No. 5311 301) packed with polystyrene based superficially sulfonated cation exchanger, (ion-exchange capacity: 0.041 mequiv./volume ml of packed column), a CDM conductivity detector and a W+W Electronics (Switzerland) data module recorder. The volume capacity of the

separator column was estimated by equilibrating the column with hydrochloric acid and after washing with water, passing standardized sodium hydroxide solution. The void volume of the system was determined by injection of high purity water to the acidified ethylenediamine eluent. All samples were analyzed in triplicate at a flow-rate of 1.5 ml/min.

3.3. Titration method and reagents

Solutions containing known concentrations of calcium and magnesium in various ratios were titrated for the sum of these two components with disodium dihydrogen ethylenediaminetetraacetate (EDTA) as a titrant in the presence of Eriochrome Black T as an indicator at pH 10. The next step of the titration method was a direct titration of calcium in another aliquots in the presence of Murexide (ammonium purpurate) indicator at pH 12. Because the first titration of solution containing calcium and magnesium gives the sum of two elements, the direct titration of calcium provides the magnesium by difference. Calcium and magnesium separations were not necessary. In the procedure the pH was adjusted to 10 by use of ammoniacal buffer solution and to 12 by use of alkaline solution. Aliquots of 50.00 ml of standard solutions were pipetted and diluted to approximately 100 ml, buffer and three drops of indicator were added and the solution was titrated by 0.005 M EDTA.

4. Results and discussion

4.1. Determination of ion chromatographic selectivity coefficients

The multiple eluent species retention model is proposed as a means of considering all competing eluent ions by taking into account their differing ion-exchange selectivities. Modelling of the observed retention behaviour by this model requires determination and evaluation of analyte/eluent and inter-eluent selectivity coefficients. These parameters may be obtained from observed retention data. The data set of measured retention volume and eluent composition (pH, concentration) can be substituted into Eq. (5), thereby producing a set of retention equation

for each mobile phase examined. Thus, the elution data set for separated ions (Mg^{2+} , Ca^{2+} , Sr^{2+}) produce a series of retention equations wherein the ion specific and intereluent selectivity coefficients are the only unknowns. The series of selectivity data can then be determined by iterative minimisation using a nonlinear algorithm. During the calculation, the sum of squares of the difference between the calculated and observed retention data was minimized.

Both the concentration of ethylenediamine and pH of the eluent have been varied in a practical range of 0.5–2.0 mM En and at acidic interval within the pH range 4–6. The samples were eluted at 12 different eluent compositions. Thus, 12 retention data were obtained for calculation of ion specific coefficients of each analyte ions (Mg^{2+} , Ca^{2+} , Sr^{2+}) and all the 36 retention data for evaluation of intereluent coefficients. The resultant values of the selectivity data and their standard deviations are shown in Table 1. Knowledge of selectivity of stationary phase may be an important component of the information required for column selection and to optimise separations. Since $K_{\text{EnH}_2^+/\text{EnH}^+}$ and $K_{\text{H}^+/\text{EnH}^+}$ intereluent coefficients are property of the mobile and stationary phase system, the values determined at different analyte ions do not deviate from one another. The coefficients are independent of alkaline earth ions to be separated. However, the values of intereluent coefficients (18.6 vs. 0.63), which indicate the selectivity difference between the divalent and monovalent eluent species, confirm that the EnH_2^{2+} component plays more important role in the separation than both EnH^+ or H^+ ions. As can also be seen in Table 1, the ion specific coefficients for separated cations reflect the expected elution order of

Table 1
Selectivity data obtained from the experimental results by iterative calculations

Analyte	Selectivity coefficients		
	$K_{\text{M}/\text{EnH}}$	$K_{\text{EnH}_2/\text{EnH}}$	$K_{\text{H}/\text{EnH}}$
Mg^{2+}	2.4±0.3	19.3±0.5	0.66±0.04
Ca^{2+}	4.8±0.1	18.7±1.6	0.57±0.04
Sr^{2+}	5.5±0.6	18.0±1.6	0.66±0.01
Mean±SD		18.6±1.3 ^a	0.63±0.05 ^a

^a All the 36 data evaluated.

alkaline earth ions with larger K_{M/EnH^+} being indicative of a larger retention volume.

4.2. Prediction of retention data using the model

Retention model was used to predict retention volume for Mg^{2+} , Ca^{2+} , Sr^{2+} ions using each of the eluent composition and all the selectivity data. Table 2 shows a set of results for alkaline earth ions. The observed retention volumes are shown, as well as those predicted by Eq. (5). From the results we also calculated the difference between the observed and the predicted retention values ($|\Delta| \% = 100|V_{R,calc} - V_{R,meas.}|/V_{R,meas.}$) both for the individual deviations and for all the data set. The average of the mean values of deviations at separated ions is 4.8% (3.6; 6.8 and 4.0%) suggesting that no significant skew exists in the comparison. This conclusion is also supported by the good agreement between the measured and calculated capacity factors in Fig. 2. The slope of the $\log k'_{calc}$ vs. $\log k'_{meas.}$ function is 0.974. The correlation coefficient calculated for all data pairs is 0.988, which confirms the predictive power of the model.

Using the calculated results for wide range of eluent composition (c_{En} and pH) it is possible to build up three-dimensional retention surface (see Fig. 3). Fig. 3 shows the simulated retention behaviour of Sr^{2+} ions based upon Eq. (5) and also some mea-

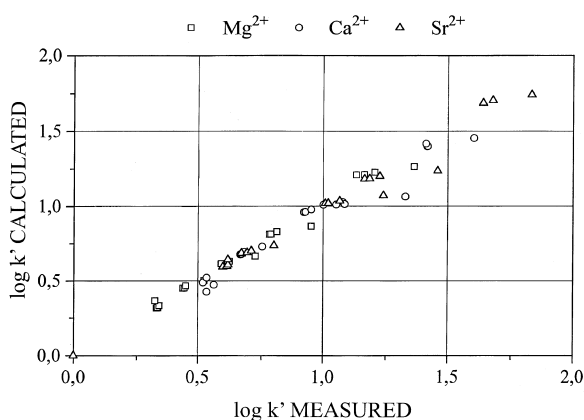


Fig. 2. Relationship of measured and calculated capacity factors for alkaline earth ions eluted with acidified ethylenediamine (slope, 0.974; correlation coefficients, 0.988).

sured retention data points. Partial molar fractions (Φ) of ethylenediamine are also illustrated as functions of pH (right panel). As an example from the right part of the figure it is shown that the value of the molar fraction (Φ) of diprotic eluent component is 1 (or percentage 100%) at pH 3. This value together with the total concentration of c_{En} (0.1 mM), determines the value of the capacity factor ($\log k' = 2.0$) by use of Eq. (5). Close examination of this figure highlights some interesting aspects of the retention characteristic of solute cations. As we can see the capacity factor of a solute ion is governed

Table 2
Comparison of measured and calculated retention volumes (ml)

c_{En} (mM)	pH	Mg^{2+}			Ca^{2+}			Sr^{2+}		
		$V_{R(meas.)}$	$V_{R(calc.)}$	$ \Delta \%$	$V_{R(meas.)}$	$V_{R(calc.)}$	$ \Delta \%$	$V_{R(meas.)}$	$V_{R(calc.)}$	$ \Delta \%$
0.5	4.0	4.49	4.68	4.2	8.53	9.26	8.5	10.29	10.45	2.0
	4.5	4.50	4.69	4.2	8.64	9.29	7.5	10.52	10.48	0.4
	5.5	4.76	4.83	1.5	9.09	9.61	5.7	11.57	10.85	6.3
	6.0	5.78	5.15	10.9	12.00	10.40	13.3	14.00	11.69	16.5
1.0	4.0	3.43	3.49	1.7	5.15	5.26	2.1	5.20	5.31	2.1
	4.5	3.47	3.50	0.9	5.20	5.28	1.5	5.30	5.36	1.1
	5.5	3.50	3.59	2.6	5.31	5.44	2.4	5.60	5.52	1.4
	6.0	3.98	3.82	4.0	6.10	5.82	4.6	6.60	5.91	10.4
2.0	4.0	2.87	2.81	2.1	4.00	3.40	15.0	4.54	4.50	0.9
	4.5	2.90	2.82	2.8	4.26	3.64	14.5	4.54	4.51	0.7
	5.5	2.92	2.88	1.4	3.95	3.75	5.0	4.71	4.63	1.7
	6.0	2.84	3.04	7.0	4.05	3.98	1.7	4.71	4.94	4.9
Mean				3.6%			6.8%			4.0%

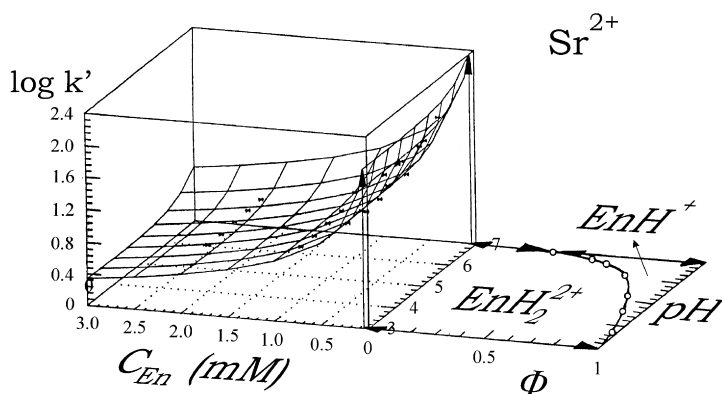


Fig. 3. Calculated retention surface and measured data points (*) for strontium ions. Panel right: Partial molar fractions of eluent components as function of actual eluent pH.

mainly by the eluent concentration and weakly by the eluent pH. The effect of pH on retention is based on protonation equilibrium of ethylenediamine. The change in the molar fractions of monoprotic (EnH^+) and diprotic (EnH_2^{2+}) eluent species as a function of pH results in change of the capacity factor for analyte ions. Increase in eluent pH ($\text{pH} > 5$) leads to an increase in the retention because the predominate form of eluent species is the monovalent at this pH interval. Decreasing the $\text{pH} < 5$ will decrease the retention. This is because the eluent is converted into diprotic form, which represents a higher selectivity component of the system. Changing the pH has a relatively limited effect on retention at the pH 4–6 interval (in that Φ changes by $\sim 15\%$), however this parameter is useful for the adjustment of retention.

The above data (predicted vs. measured) strongly suggests that the separation of alkaline-earth ions takes place by an ion-exchange mechanism alone, governed by the high selectivity of ethylenediammonium cations.

4.3. Comparative analyses of calcium and magnesium

The simultaneous nature, speed and selectivity of the method, gives the chromatography several advantages over classical titrimetry for the determination of Ca^{2+} , Mg^{2+} ions. However complexometric titrimetry is a standard method for the estimation of calcium and magnesium in water samples. The most familiar of complex-forming species is EDTA. It is

possible, by using EDTA, to carry out accurate and reliable titrations of alkaline earth ions, selectivity usually being achieved by suitable pH control and indicators. Although the titration method is time consuming, especially with two steps determination involved, it is, however, useful for comparison of the IC results when independent method is required for control of the quality of analytical work.

Statistical analysis was performed to test the two methods when applied to determination of calcium and magnesium. The sum of calcium and magnesium was maintained at a constant value (1 mmol) with various molar ratio of the components in standard solutions. Fig. 4 shows some typical chromatograms obtained using En eluents and different composition of samples. The concentration of Ca^{2+} and Mg^{2+} were varied from 0.1 to 0.9 mM and were determined under identical IC conditions. Three replicate runs are shown for all separations in Fig. 4a, b and c. As can be seen from the figures the areas and shapes of the induced peaks were virtually identical when the molar concentrations were the same. Similarly nine standard samples were also analyzed by complexometric titration under the conditions described above in Section 3.3.

A comparison of the results for the determination of Ca^{2+} and Mg^{2+} ions using ion chromatography and titration are shown in Table 3 and Fig. 5, respectively. In the present set of standard samples, the molar ratio of alkaline earth ions varies from 1 to 9. The results of analysis showed good agreement between the values (mean $|\Delta| \leq 2.65\%$) obtained by

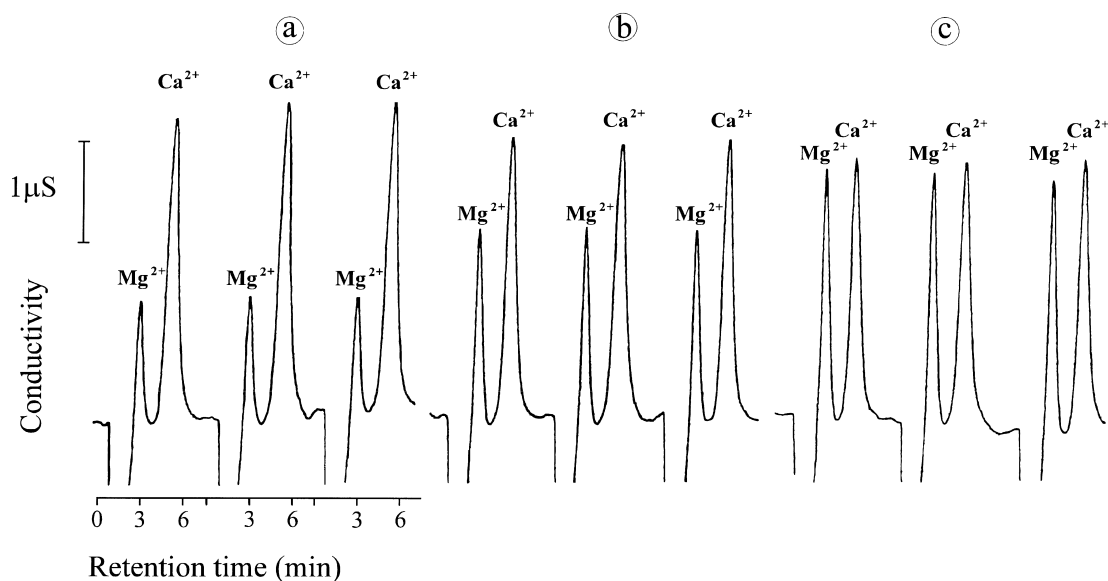


Fig. 4. Three replicate runs for Ca^{2+} , Mg^{2+} IC separations with various molar (mM) ratio of the components, $[\text{Mg}^{2+}]/[\text{Ca}^{2+}] = 2/8$ (a); $[\text{Mg}^{2+}]/[\text{Ca}^{2+}] = 3/7$ (b); $[\text{Mg}^{2+}]/[\text{Ca}^{2+}] = 4/6$ (c). Eluent: $5 \cdot 10^{-1}$ mM ethylenediamine, pH 4.0, conductivity detection.

the comparative methods (Table 3). This conclusion is also supported by the comparative relationship of Fig. 5. For Ca^{2+} ions, the negative deviation increases slightly with increasing Mg^{2+} concentrations of the sample in complexometric titrations (see Table 3) due to the adjustment of the pH for Ca^{2+} direct measurement. This value (pH 12) causes precipitation of magnesium hydroxide and calcium is

adsorbed on the surface of the resulting precipitate. Similarly, when calcium is titrated directly, strontium and barium will also cause some interference at high pH values. The volumetric method is more strongly affected by the sample matrix. As shown in Fig. 6 adequate resolution and fast separation were obtained without matrix interferences using 1.0 mM ethylenediamine as eluent.

Table 3

Comparative data: Ion chromatography (IC) versus complexometric titration (CT)

Sample composition ($\cdot 10^{-4}$ M)		Δ -IC (%)		Δ -CT (%)	
Mg^{2+}	Ca^{2+}	Ca^{2+}	Mg^{2+}	Ca^{2+}	Mg^{2+}
1	9	+0.55	+0.21	+1.57	+3.90
2	8	-0.82	+1.83	-0.41	-6.50
3	7	-0.23	-2.65	-0.67	+1.69
4	6	+0.55	+1.02	-0.36	-2.60
5	5	-0.13	0.00	-0.33	+2.18
6	4	+1.06	+0.13	-0.78	+0.32
7	3	-0.22	+0.23	-1.86	+2.54
8	2	-4.40	-0.69	-1.03	+2.65
9	1	+5.90	+0.35	-2.52	+1.49
Mean $ \Delta $		1.54	0.55	1.06	2.65

A series of standards of Ca^{2+} and Mg^{2+} (taken) were analysed by IC and CT (found) using the analytical conditions in the 3. Experimental section. Δ (%) = $100 (c_{\text{found}} - c_{\text{taken}}) / c_{\text{taken}}$; IC = ion chromatography, CT = complexometric titration, mean $|\Delta|$ = mean of absolute differences.

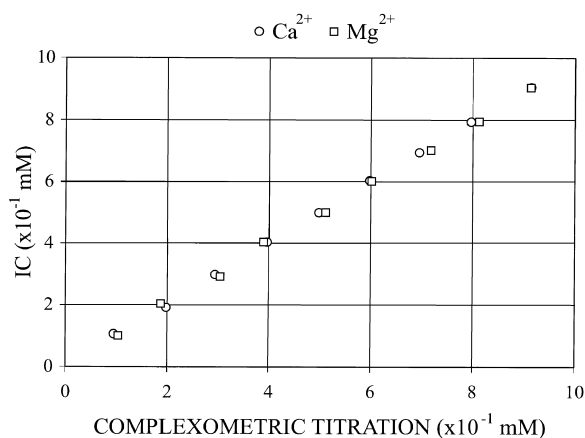


Fig. 5. Comparison of the results for the determination of Ca^{2+} and Mg^{2+} using ion chromatography (IC) and complexometric titration (CT) (slope, 0.980; correlation coefficient, 0.999).

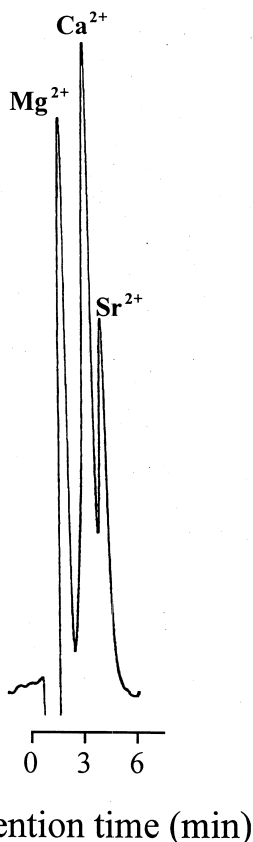


Fig. 6. Separation of alkaline earth ions. Eluent: 1 mM ethylenediamine, pH 4.0, conductivity detection. Solute concentrations are 30 mg/l for magnesium and calcium, 100 mg/l for strontium.

5. Conclusion

The ability of multiple eluent species model allows the analyst to describe and to predict the retention characteristics of alkaline-earth cations eluted by acidified ethylenediamine. Predictive capabilities of retention model can be used to simplify the separation development in cation analysis. The selectivity of the system is directly related to the simultaneous ion-exchange competition of analyte/eluent components and can be explained in terms of the equilibrium model. The results suggests that the IC can be applied to a routine analysis of alkaline-earth metals and the method gives several advantages over volumetric method (multi-ion analysis, speed and selectivity, μl sample volume, limited matrix effect).

Acknowledgements

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