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ELUENT SELECTION FOR THE DETERMINATION OF CATIONS IN ION CHROMATOGRAPHY

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SUMMARY

Literally thousands of eluent types can be used to separate ions in chromatography. Eluents are chosen and modified based on the interaction of the eluent and sample cations with the column. Cations can be separated by differences in their affinities for the column. Sample affinities are affected by ionic charge, eluent concentration and several other parameters. Cation separations can also be performed using complexing reagents to control selectivity.

INTRODUCTION

Ion chromatography is a powerful analytical tool for the analysis of ionic and polar substances. It is a tool that can separate and detect a wide variety of substances using essentially the same technique.

Basically, three parameters can be changed when choosing conditions for an ion chromatographic separation: the detector, column, and eluent. There are perhaps three or four popular detector types. Manufacturers now offer dozens of different columns for performing separations. But the choice of the eluent may be considered to be the most powerful parameter. There are literally thousands of eluent conditions that can be chosen for any particular column and detector combination. Not only can the type of eluent be changed, but its pH and concentration can be varied in almost infinite proportions.

Several workers have described the role of the eluent in the ion chromatography of anions^{1–5}. Relatively little work has been performed on the role of the eluent in the ion chromatography of cations^{6,7}. The purpose of this paper is to provide a theoretical approach as well as a practical approach to the selection of eluents for cation chromatography. Much of cation chromatography is performed with cation-exchange columns. The interaction of the ion-exchange column with the eluent are studied in this paper. Previous work has shown that complexing reagents can be added to the eluent to control separations⁷. Factors affecting the use of complexing reagents and the different ways they can be used are shown in this paper.

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EXPERIMENTAL

Apparatus

The instrument used for this work was a Wescan Instruments Model 266 ICM ion chromatographic system. The Rheodyne Model 7025 injector was equipped with a 100- μ l injection loop. All chromatograms were obtained at room temperature.

Column

Wescan cation columns Cat. No. 269004 and 269024 were used for this work. The columns have dimensions of 10 cm \times 3.2 mm and 5 cm \times 4.6 mm, respectively. The columns contain beads of surface sulfonated poly(styrene-divinylbenzene) with a capacity of 0.04 mequiv./g. A silica-based Cation/S column (5 cm \times 4.6 mm) was also used. The substrate of this material is porous silica. A polymer containing sulfonic acid groups is bonded to the silica.

Reagents

The nitric acid used in this work was Ultrex grade or any grade that contained a minimum amount of divalent metals. All other chemicals used were reagent grade or better.

DISCUSSION

The separation of cations in a chromatographic system can be performed based on either of two concepts. Sample cations can be separated on a column based on affinity differences of sample cations for the column. Sample cations can also be separated by using complexing reagents in the eluent to change the form of the cation.

Separations based on affinity differences

Theory. As sample and eluent ions flow through a cation-exchange column, the ions compete to interact at the ion-exchange sites. Separations based on affinity differences result from differences in the relative attraction of sample ions and the eluent ions for the ion-exchange functional group.

Cation separations based on affinity differences are also affected by relative sample and eluent charge, eluent concentration, and eluent pH. The theoretical basis for this behavior can be shown by studying ion-exchange equilibria. It is well established that ion-exchange reactions are reversible; therefore, ion-exchange behavior can be described in terms of equilibria equations¹.

For monovalent charged ions:



and for multivalent charged ions:



The subscripts s and r denote the solution and the resin phase, respectively; *a* is the charge of anion A and *b* is the charge of anion B. The equilibrium constants for these equilibria equations are

$$K_B^A = \frac{[A_r^-][B_s^-]}{[A_s^-][B_r^-]} \quad (2a)$$

$$K_B^A = \frac{[A_r^{a-}]^b [B_s^{b-}]^a}{[A_s^{a-}]^b [B_r^{b-}]^a} \quad (2b)$$

For simplicity, only ion concentrations are used and the technically correct ion activities will not be considered. The equilibrium constant for any particular cation pair is called a selectivity coefficient.

A separation on a chromatographic column can be thought of as a series of equilibrium reactions. Using chromatographic theory, it has been shown that the equilibrium equation can be rearranged to predict behavior in cation-exchange chromatography^{1,7}. The result is shown by

$$\log k = \frac{a}{e} \log C - \frac{a}{e} \log E + \frac{1}{e} \log K_E^A - \frac{a}{e} \log e + D \quad (3)$$

where k is the cation capacity factor, a is the charge of the sample cation, e is the charge of the eluent cation, C is the resin capacity, and E is the eluent concentration.

TABLE I

CAPACITY FACTORS FOR VARIOUS CATIONS ON A 0.06 mequiv./g CATION EXCHANGER USING A PERCHLORIC ACID ELUENT

Data derived from ref. 8.

Cation	Perchloric acid concentration				
	1.00 M	0.75 M	0.50 M	0.25 M	0.10 M
Mg ²⁺	0.16	0.26	0.50	1.38	7.42
Ca ²⁺	0.32	0.56	1.46	5.93	21.2
Sr ²⁺	0.44	0.80	2.04	8.46	35.0
Ba ²⁺	1.00	1.50	4.90	15.6	
Fe ²⁺	0.16	0.26	0.56	1.92	9.10
Hg ²⁺	0.16	0.30	0.68	2.96	11.6
Mn ²⁺	0.16	0.26	0.54	2.00	12.0
Zn ²⁺	0.12	0.30	0.70	2.52	12.5
Ni ²⁺	0.16	0.28	0.58	2.00	12.6
Cu ²⁺	0.16	0.32	0.60	3.16	12.7
V ⁶⁺	0.16	0.28	0.66	3.48	12.7
Zr ⁴⁺	0.14	0.24	0.64	1.98	13.2
Co ²⁺	0.20	0.28	0.48	2.00	13.4
Cd ²⁺	0.22	0.32	0.76	2.52	25.0
Pb ²⁺	1.20	1.88	4.70	28.2	99.0
Al ³⁺	0.68	1.58	5.22	42.6	
V ³⁺	1.12	2.86	10.0		
In ²⁺	1.14	3.02	10.4	63.2	
Fe ³⁺	1.06	2.86	9.86	79.2	
Bi ³⁺	8.66	21.0	53.2		

The constant D includes terms specific to a particular ion-exchange resin and column. These terms include the column void volume and resin density.

Effect of ion charge and eluent concentration. The validity of eqn. 3 depends to a large extent on the ability of the ion exchanger to interact with multivalent cations. Sevenich⁸ tested the equation by plotting $\log k$ vs. $\log E$ for a series of transition and rare earth metals eluted with an acid eluent at various concentrations. Retention data are shown in Tables I and II. Assuming the resin capacity and selectivity coefficient in eqn. 3 remain constant, the slope of the plot should be minus the ratio of sample charge to eluent charge. The results of these plots, listed in Tables III and IV, show that in most cases the correlation is quite good.

There are some interesting exceptions. The largest deviation from theory appears to occur with large hydrated cations. For example, deviation decreases in the order $\text{Mg}^{2+} > \text{Ca}^{2+} > \text{Sr}^{2+} > \text{Ba}^{2+}$. The diameter of the hydrated cation decreases in the same order. The large radius of hydrated Mg^{2+} may prevent the cation from penetrating the ion exchanger and exchanging with two functional groups. This is shown in Fig. 1. If the ion-exchange groups are not completely accessible, then the divalent cation may not be able to bind to two functional groups and establish complete exchanger/sample cation charge neutrality. It may be able to bind to only one ion-exchange site. Thus, the effective charge of the sample cation is lower. Since the eluent cation, the hydronium ion, is monovalent, its effective charge cannot be reduced. The result of an effective reduced charge of the sample cation is a reduced slope of the $\log k$ vs. $\log E$ plot.

Fortunately, the deviations from theory are slight. Even less deviation is observed when the eluent structure is closer to that of the sample cations. This is shown in Tables V and VI where the eluent is a divalent magnesium cation. In most cases

TABLE II

CAPACITY FACTORS FOR RARE EARTH CATIONS ON A 0.06 mequiv./g CATION EXCHANGER USING A PERCHLORIC ACID ELUENT

Data derived from 8.

Cation	Perchloric acid concentration					
	1.00 M	0.85 M	0.75 M	0.60 M	0.50 M	0.40 M
Lu^{3+}	2.64	4.66	6.50	12.9	26.8	50.0
Yb^{3+}	2.90	5.10	7.10	14.0	28.4	52.0
Tm^{3+}	1.47	5.20	7.46	14.6	28.6	56.4
Y^{3+}	3.10	5.88	8.10	16.2	29.8	59.0
Er^{2+}	3.14	5.26	7.94	15.6	30.2	59.2
Ho^{3+}	3.22	5.56	8.50	16.5	32.6	62.8
Dy^{3+}	3.74	6.04	9.16	18.4	34.4	70.2
Gd^{3+}	4.84	8.32	12.4	24.4	47.2	90.4
Eu^{3+}	5.40	9.16	13.7	27.2	52.4	104
Sm^{3+}	5.98	11.3	15.3	30.0	58.8	115
Nd^{3+}	7.06	13.5	17.6	35.0	68.6	136
Pr^{3+}	7.40	14.1	18.4	37.2	70.6	140
Ce^{3+}	8.60	14.3	21.0	42.8	80.0	166
La^{3+}	9.58	15.5	23.6	47.4	98.8	186

TABLE III

SLOPES OF PLOTS OF $\log k$ OF TRANSITION METAL CATIONS vs. \log CONCENTRATION (MULTIPLIED BY ACTIVITY COEFFICIENT) OF PERCHLORIC ACID ELUENT

Data derived from ref. 8.

<i>Cation</i>	<i>Slope</i>	<i>Cation</i>	<i>Slope</i>
Mg ²⁺	-1.66	Zn ²⁺	-1.98
Ca ²⁺	-1.87	Ni ²⁺	-1.87
Sr ²⁺	-1.91	U ⁶⁺	-1.96
Ba ²⁺	-1.97	Cu ²⁺	-1.92
Al ³⁺	-2.88	Fe ²⁺	-1.79
Bi ³⁺	-2.67	Co ²⁺	-1.86
Fe ³⁺	-2.99	Cd ²⁺	-2.08
In ³⁺	-2.78	Pb ²⁺	-2.00
Y ³⁺	-2.95	Hg ²⁺	-1.92
Mn ²⁺	-1.89	Zr ⁴⁺	-1.95

the slopes are unity as predicted by theory. However, there are two cases where the slope is greater than 1, again suggesting less penetration of Mg²⁺ into the cation exchanger compared to the competing cation. In this case the slope is greater than predicted because Mg²⁺ is the eluent.

The practical applications of this work are twofold. First, since divalent and trivalent cations are affected differently by eluent concentration, it is possible to change relative retention times simply by changing the eluent concentration. As the eluent concentration is increased, trivalent cations are shifted to shorter retention times faster than divalent cations (Fig. 2).

The second practical application has to do with how eluent charge affects the eluent concentration needed to produce the desired separation. Tables I and V show that a Mg²⁺ eluent can produce roughly the same retention times as a hydronium ion eluent with a factor of about twenty five lower eluent concentration. On the other

TABLE IV

SLOPES OF PLOTS OF $\log k$ OF RARE EARTH METALS vs. \log CONCENTRATION (MULTIPLIED BY ACTIVITY COEFFICIENT) OF PERCHLORIC ACID ELUENT

Data derived from ref. 8.

<i>Cation</i>	<i>Slope</i>	<i>Cation</i>	<i>Slope</i>
Lu ³⁺	-3.01	Gd ³⁺	-2.99
Yb ³⁺	-2.95	Eu ³⁺	-3.01
Tm ³⁺	-2.99	Sm ³⁺	-2.97
Y ³⁺	-2.95	Nd ³⁺	-2.97
Er ³⁺	-2.95	Pr ³⁺	-2.95
Ho ³⁺	-3.01	Ce ³⁺	-3.01
Dy ³⁺	-3.01	La ³⁺	-3.04
Tb ³⁺	-3.02		

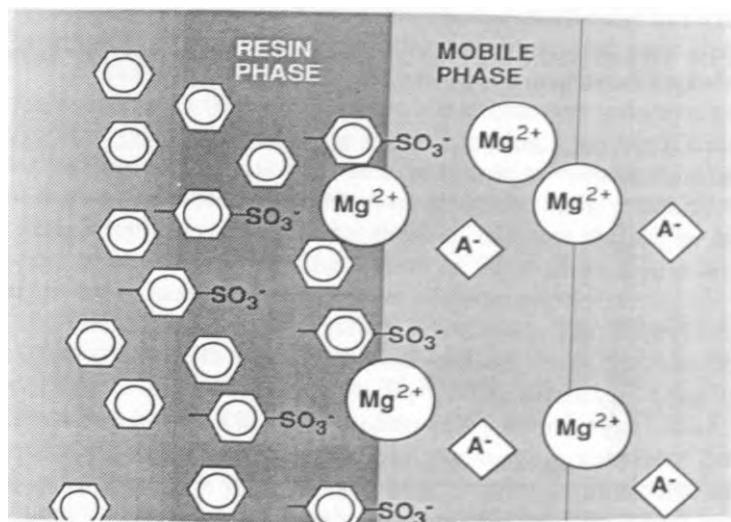


Fig. 1. The validity of eqn. 3 depends on the placement of the functional groups in the cation-exchange matrix and the ability of the sample cation to react with the cation exchanger.

hand, an acid eluent is quite effective in eluting monovalent cations such as alkali metals and amines (Table VII).

A general rule in choosing an eluent for affinity type separations might be "like elutes like". Of course with the proper detector, it may be possible to use eluent gradients to elute a wide variety of sample cations⁹.

TABLE V

CAPACITY FACTORS OF VARIOUS CATIONS ON A 0.06 mequiv./g CATION EXCHANGER FOR A MAGNESIUM PERCHLORATE ELUENT

Data derived from ref. 8.

Cation	Magnesium concentration			
	10.0 mM	5.00 mM	1.00 mM	0.500 mM
V ⁴⁺	0.66	1.58	7.30	13.2
Zn ²⁺	1.36	2.75	12.9	24.6
Co ²⁺	1.54	3.06	14.0	25.2
Fe ²⁺	1.42	3.00	13.5	25.8
Ni ²⁺	1.44	3.06	13.9	26.4
Cu ²⁺	1.90	3.62	15.7	26.4
Zr ⁴⁺	1.56	3.08	14.2	27.0
Hg ²⁺	1.48	3.12	14.4	27.4
Mn ²⁺	1.64	3.36	15.3	29.4
Cd ²⁺	1.02	2.50	15.6	33.0
U ⁶⁺	2.76	5.84	21.8	37.8
Pb ²⁺	12.9	31.6		

TABLE VI

SLOPES OF PLOTS OF $\log k$ OF METAL CATIONS vs. \log CONCENTRATION (MULTIPLIED BY ACTIVITY COEFFICIENT) OF MAGNESIUM PERCHLORATE ELUENT

Data derived from ref. 8.

Cation	Slope	Cation	Slope
V ⁴⁺	-0.990	Zr ⁴⁺	-0.951
Zn ²⁺	-0.934	Hg ²⁺	-0.969
Co ²⁺	-0.936	Mn ²⁺	-1.156
Fe ²⁺	-0.960	Cd ²⁺	-0.958
Ni ²⁺	-0.964	U ⁶⁺	-0.861
Cu ²⁺	-0.886	Pb ²⁺	-1.288

Effect of eluent pH. One of the most popular eluents for cation-exchange work is a mixture of ethylenediamine and an acid to produce an ammonium type eluent. Ethylenediamine is dibasic; therefore, depending on the eluent pH, the eluent may be monovalent, divalent or a mixture of the two valences. As shown above, eqn. 3 predicts behavior for pure monovalent eluents or pure divalent eluents. However, the selectivities of monovalent and divalent eluent anions are different for the two different eluent forms. In this case eqn. 3 is expanded as shown in eqn. 4.

$$\log k = \frac{a}{e_1} \log C_1 + \frac{a}{e_2} \log C_2 - \frac{a}{e_1} \log E_1 - \frac{a}{e_2} \log E_2 + \frac{1}{e_1} \log K_{E_1}^A + \frac{1}{e_2} \log K_{E_2}^A + D' \quad (4)$$

where the subscripts 1 and 2 denote the monovalent and divalent eluent, respectively. Obviously, the equation becomes quite cumbersome. However it can be simplified.

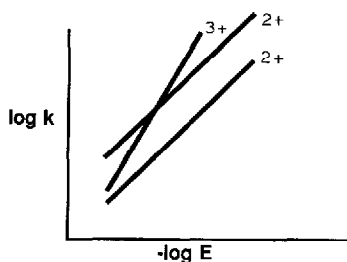


Fig. 2. As the eluent concentration is increased, the retention times of cations become shorter. Divalent cations are affected equally. A plot of $\log k$ vs. $\log E$ for two different divalent cations results in a parallel plot. However, increasing eluent concentration shifts the retention of a trivalent cation to shorter times faster than divalent cations.

TABLE VII

CAPACITY FACTORS OF ALKALI METALS AND AMINES ON CATION EXCHANGERS WITH 3.00 mM NITRIC ACID ELUENT

	<i>Resin-based Wescan 269024</i>	<i>Silica-based Wescan 269041</i>
Li ⁺	4.63	2.32
Na ⁺	7.00	3.05
NH ₄ ⁺	11.5	4.29
K ⁺	15.0	5.47
Ethanolamine	11.5	5.34
Diethanolamine	11.5	8.95
Triethanolamine	11.5	13.34
Methylamine	9.60	6.87
Dimethylamine	11.9	11.73
Trimethylamine	17.9*	**
Decylamine	**	**
Ethylenediamine	**	**
Cyclohexylamine	15.03*	38.9***
Morpholine	15.2*	16.7
Aminomethyl propanol	8.77	9.97
Diethyl ethanolamine	13.35	**
Dimethylamino 2-propanol	10.59	20.40*
Octylamine	**	**
Urea	**	**
Rb ⁺	16.25	6.32
Cs ⁺	17.70	8.33

* Slight-tailing.

** No peak.

*** Tailing.

Making the assumption that only the divalent form of the eluent contributes to the eluting power of the eluent, the equation can be simplified to

$$\log k = -\frac{a}{e_2} \log E_2 + D'' \quad (5)$$

Experiments were performed to test eqn. 5. A series of eluents were prepared that contained a constant 1 mM concentration of ethylenediamine. Various amounts of nitric acid were added to the eluent solutions to form all +1 charged eluent cations, all +2 charged eluent cations, and several mixtures of the two states. Log k vs. log E_2 were plotted for Mg²⁺, Ca²⁺ and Sr²⁺ sample cations. The results are shown in Fig. 3. In all cases linear plots were obtained. The slopes of the plots were slightly higher than expected: Mg²⁺, -1.14; Ca²⁺, -1.11; and Sr²⁺, -1.17. It was impossible to elute any of the sample cations with the pure monovalent form of the eluent. However, when even a small fraction of the eluent was divalent, elution of the sample cations was achieved.

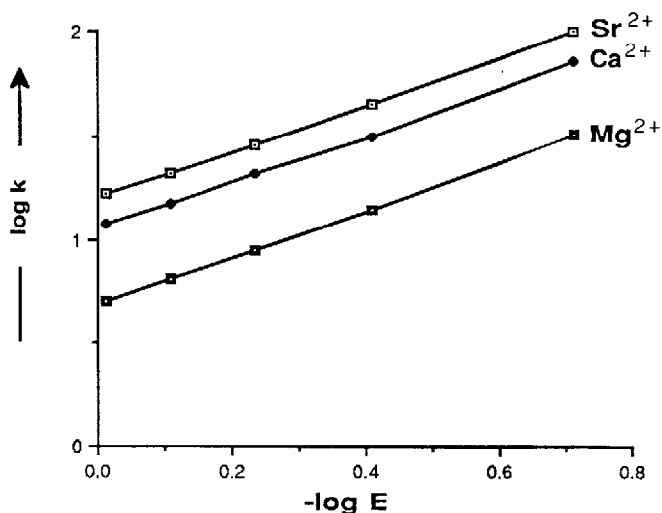


Fig. 3. Plot of $\log k$ of three alkaline earth metals vs. \log concentration of the divalent form of the ethylenediammonium eluent. The monoprotonated ethylenediamine concentration is ignored.

Effect of organic solvent. The selectivity of cation-exchange columns can be adjusted by the addition of an organic modifier to the eluent. The organic solvent can swell the ion exchanger and allow better functional group interaction of certain ions. For example, using a 3.2 mM nitric eluent, methylamine will coelute with K^+ (Fig. 4). However, adding 40% methanol to the eluent causes K^+ to elute later but does not affect the elution of methylamine (Fig. 5). An organic solvent may also reduce adsorption of certain ions with the organic substrate of an ion exchanger.

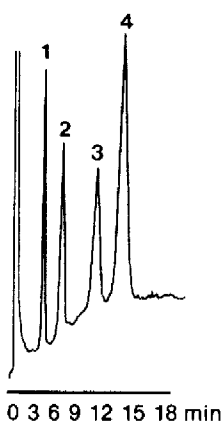


Fig. 4. Separation of monovalent cations with a 3.2 mM nitric acid eluent, pH 2.4. The eluent contains no methanol. Conditions: column, Wescan Cation Cat. No. 269004; flow-rate, 2.0 ml/min; ICM conductivity detector. Peaks: 1 = 2 ppb Li^+ , 2 = 8 ppb Na^+ , 3 = 7 ppb NH_4^+ , 4 = 40 ppb K^+ .

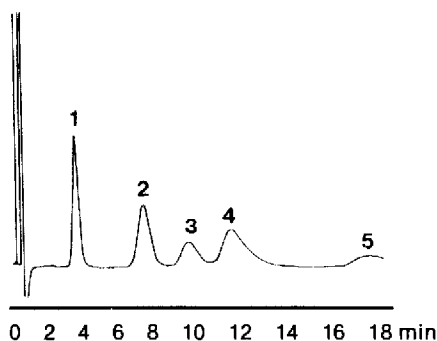


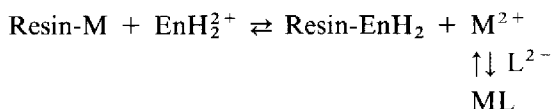
Fig. 5. Separation of monovalent cations with a 3.2 mM nitric acid eluent, containing 40% methanol. Other conditions as in Fig. 4. Peaks: 1 = 1.6 ppm Li^+ , 2 = 6 ppm Na^+ , 3 = 3 ppm NH_4^+ , 4 = 16 ppm monomethylammonium ion, 5 = 6 ppm K^+ .

Kawazu has done extensive work studying the work of organic solvents¹⁰. It should be noted that organic solvents may damage a column if the wrong type is used, or the solvent concentration is too high. A low-capacity cation-exchange column should not be stored for long periods in a solution containing an organic solvent.

Separations based on complexing reagents

Complexing anion reagents can react with metal cations to form uncharged or reduced charge metal-ligand complexes. This effect can be used in two ways. One way is to control the amount of metal cation available to exchange with a cation-exchange column. Reducing the fraction of metal in the cation form causes the sample peak to elute faster from a column. The other way is to chromatograph the uncharged metal-chelate complex on a reversed-phase column.

Cation-exchange separations. Adding a complexing ligand, L, to an eluent shifts the ion-exchange equilibrium. This is shown below where an eluent ethylenediammonium ion (EnH_2^{2+}) competes with metal (M^{2+}) for sites on the cation exchanger.



When L is added to an eluent and a metal cation is injected, part of the metal is complexed. The effective concentration of the metal cation is reduced and the metal is less successful in competing for the ion-exchange sites. This causes the metal to elute more rapidly from the column. The ligand type, concentration, and pH are selected so that the complexation of the metal cation is only partial.

Eqn. 6 predicts elution behavior when a complexing anion is present:

$$\log k = \frac{a}{e} \log \alpha_M + \frac{a}{e} \log C - \frac{a}{e} \log E - \frac{a}{e} \log e + \frac{1}{e} \log K_E^A + D \quad (6)$$

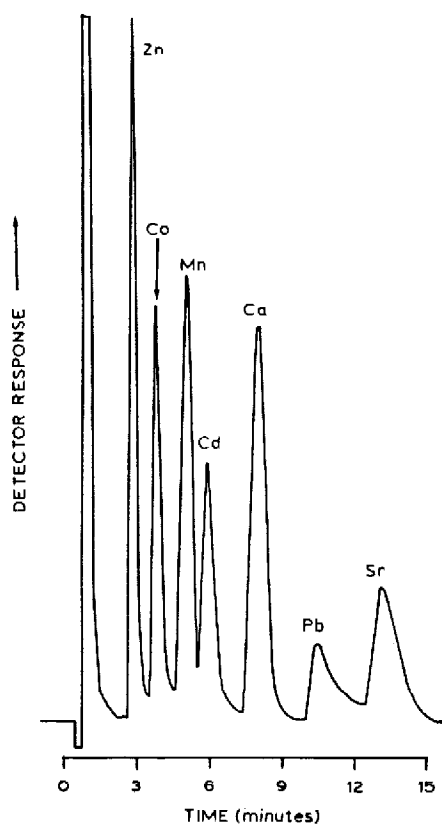


Fig. 6. Separation of divalent metal cations on a 0.06 mequiv./g cation-exchange column with a 1.5 *mM* ethylenediammonium cation and 2.00 *mM* tartaric acid eluent, at pH 4.00⁸.

where α_M is the fraction of the sample cation in solution as the uncomplexed cation. This equation has been verified by Sevenich and Fritz⁷. Complexation of the metal increases with the eluent pH and the chelating reagent concentration. Common complexing anions include tartrate, citrate, oxalate, 2-hydroxyisobutyrate and several others.

Two different approaches have been used for the complexation and elution of metal cations from a cation-exchange column. One method is called the "push-pull" approach. In this approach the elution mechanism is a combination of the mass action "pushing" effect of the eluent (ethylenediammonium) cation and weakly complexing "pulling" effect of the complexing anion. Very small amounts of complexing reagent are used and a major proportion of the separation depends on the presence of a strong driving cation. Sevenich and Fritz⁷ have studied this approach in detail. An example of separation of this type is shown in Fig. 6.

The other complexation approach uses more of a pure "pull" mechanism. In this approach, higher concentrations of complexing reagents are used and care is taken to use only a very weak driving anion. In order for a chelating (acid) reagent to be used, its pH must be adjusted to a more basic pH. Lithium hydroxide is most

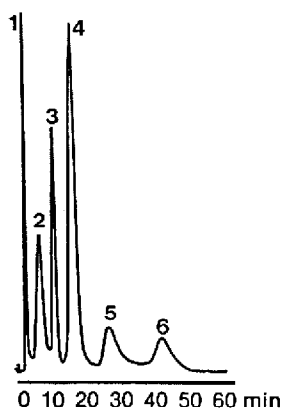


Fig. 7. Separation of transition metal cations with a 20 mM tartaric acid and 4 mM oxalic acid, pH 4 with lithium hydroxide eluent. Weakly bound cations (Fe^{3+} , Cu^{2+} etc.) are separated using a pH 2.4 eluent with the same acid concentrations. Column, Wescan Cation Cat. No. 269004; detector, Wescan Model 273 PCR, Cat. No. 273 100. Peaks: 1 = Cu^{2+} , 2 = Ni^{2+} , 3 = Zn^{2+} , 4 = Co^{2+} , 5 = Pb^{2+} , 6 = Fe^{2+} .

often used because Li^+ is a very weak driving cation and contributes very little to the chromatography. An example of a transition metal separation is shown in Fig. 7. Elchuk and Cassidy¹¹ have done some excellent work using this complexing approach. They separated the rare earth metals using a gradient of 0.17 M to 1 M 2-hydroxyisobutyric acid at pH 4.6.

Reversed-phase separations. Complexing reagents can be used to form neutral metal-chelate complexes. The chelating reagents are usually chosen so that the metal chelate can be detected by UV absorption. The organic metals complexes are then separated using conventional reversed-phase high-performance liquid chromatographic columns and detectors. This a fairly active area of chromatography and several reviews have been published¹²⁻¹⁴. The most popular chelating reagents include diethyldithiocarbamate, 4-(pyridylazo)resorcinol and 8-hydroxyquinoline. Some recent work has been published using N-methylfurohydroxamic acid to separate high valence metals such as Zr^{4+} , Hf^{4+} , Fe^{3+} , Nb^{5+} , Al^{3+} , and Sb^{3+} (ref. 15).

Usually, the metal-chelate complex is formed prior to chromatographic separation. Chelating reagent is mixed with the sample and allowed to react thoroughly before the sample is introduced into the instrument. But the sample metal-chelate complexes may not be stable in the eluent stream. Frequently, the eluent also contains a chelating reagent to maintain or control the metal-chelate complex. Metal-chelate complexes tend to form with increasing concentration of chelating reagent and higher pH. However, because very strong chelating reagents are used, the eluents tend to be acidic.

CONCLUSION

The eluent is the most powerful parameter that can be varied when devising cation separations. Cations can be separated by affinity differences or by using complexing reagents. In many cases equations can be derived which predict elution be-

havior. The ultimate goal might be to use these equations to choose elution conditions for any given desired separation. That goal is not yet realized. Nevertheless, the most important parameters affecting separations can be demonstrated. Changing the eluent type, pH, concentration, etc. can be done in a logical manner.

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