Journal of Chromatography, 602 (1992) 111–117
Elsevier Science Publishers B.V., Amsterdam

CHROMSYMP. 2492

Ion chromatography of metal cations on carboxylic acid resins

John Morris and James S. Fritz*

Ames Laboratory and Department of Chemistry, Iowa State University, Ames, IA 50011 (USA)

ABSTRACT

The goal of the present work is to study cation separations on weak-acid resins that are easily synthesized and carry the exchange group on the crosslinking benzene ring of the resin or on a short spacer arm from the ring. The synthesis and general properties of two carboxylic resins are described. A higher exchange capacity is required for effective ion chromatographic separations than that needed for sulfonated resins. A number of excellent separations are reported using eluents containing ethylenediammonium cations plus a weak complexing agent. The effect of pH on retention times of metal ions is reported.

INTRODUCTION

Perhaps the best method for separating 2+ and 3+ metal cations by ion chromatography is through the use of complexing eluents. Sevenich and Fritz [1] obtained excellent separations using an ethylenediammonium tartrate eluent in conjunction with a conductivity detector. Further selectivity is possible with the addition of a second chelating reagent (such as EDTA) to the sample only [2]. Others have obtained excellent separations of various metal ions using eluents containing tartrate, citrate, oxalate, 2-hydroxyisobutyrate, or salts of pyridyldicarboxylic acid [3–7].

Virtually all ion chromatographic separations of metal cations have been carried out on various strong-acid ion exchangers containing the sulfonic acid group. These strongly acidic ion exchangers maintain complete ionic capacity over a large pH range of 2–12. A weak-acid exchanger, such as the carboxylic acid, loses its ionic capacity as the pH goes below the $\mathrm{p}K_\mathrm{a}$ of the functional group. The pH affects the separation of the metal cations thus adding an additional parameter for optimization. Kolla *et al.* [8] prepared an efficient carboxylic acid resin by coating a polybutadiene–maleic acid resin onto the surface of 5 μm porous silica. Using this resin, they obtained simultaneous separations of monovalent and divalent cations.

The preparation and use of two new carboxylic acid resins are described in the present research. Both resins are prepared by simple Friedel–Crafts addition reactions. One has the carboxyl group attached to the benzene ring of a spherical polystyrene–divinylbenzene (PS–DVB) resin via a spacer arm of three carbon atoms. The carboxyl group is attached directly to the benzene ring in the other resin. Excellent ion chromatographic separations of metal ions are possible using these resins in conjunction with any of several complexing eluents.

EXPERIMENTAL

Apparatus

The chromatographic system consisted of several components. An Eldex model AA-94 pump (Eldex Labs, Menlo Park, CA, USA) set to deliver eluent at a flow-rate of 1.0 ml/min, a 7125 Rheodyne injector (Rheodyne, Berkeley, CA, USA) equipped with a 10-μl loop, a Wescan ICM II ion analyzer (Wescan Instruments, Santa Clara, CA, USA) with conductivity detection at a constant temperature, a

0021-9673/92/$05.00

Fisher Recordall series 5000 recorder (Fisher Scientific/Instrument Lab., Itasca, IL, USA) and a Hitachi D-2000 integrator (EM Science, Cherry Hill, NJ, USA) were used for all separations. A Shandon HPLC packing pump (Shandon Southern, Sewichley, PA, USA) was used for column packing.

Reagents and chemicals

The spherical PS–DVB resins (Sarasep, Santa Clara, CA, USA) used in this experiment consisted of two sizes; 10-μm resin with 80 Å pore size and 415 m^2/g surface area, and 5-μm resin with similar pore size and surface area. The resin was washed with water, acetonitrile and methanol, and then dried.

The reagents and solvents used for the derivatization reactions were reagent grade. Stock solutions of the metals were prepared from reagent-grade chloride salts. The concentrations of metal ions in the salt solutions injected ranged from $1.2 \cdot 10^{-4}$ to $1.1 \cdot 10^{-3}$ *M*. Eluents were prepared daily using reagent-grade solutions of ethylenediamine and the specified organic acid. A Barnstead Nanopure II system (Sybron Barnstead, Boston, MA, USA) was used to further deionize distilled water for all eluents and sample mixtures. Adjustments in pH were made with reagent grade solutions of sodium hydroxide and hydrochloric acid.

Synthetic procedures

The carboxylic acid functional groups were introduced into the benzene ring of PS–DVB resins by the following procedures:

(1) $-COCH_2CH_2CO_2H$ *derivative (resin I).* Mix 2.5 g of resin with 3.6 g of succinic anhydride and 50 ml of tetrachloroethane in a 100-ml round-bottomed flask. Stir for 15 min, then add 10.7 g of anhydrous aluminum chloride and reflux at 45°C for 24 h. Pour the product into a methanol–ice solution to quench the reaction. Collect the resin by filtration, wash with methanol, 1 *M* hydrochloric acid and water, then dry. The exchange capacity was found to be 0.60 mequiv./g by acid–base titration of the carboxylic acid.

(2) $-CO_2H$ *derivative (resin II).* Mix 2.5 g of resin with 8.0 ml of phenyl chloroformate and 50 ml of tetrachloroethane in a 100-ml round-bottomed flask. Stir for 15 min, then add 10.0 g of anhydrous aluminum chloride and reflux at 100°C for 4 h. Pour the product into a methanol–ice solution. Isolate the resin, wash with methanol, then dry. Hydrolysis of the ester is accomplished by refluxing the resin for 1 h in a 1 *M* sodium hydroxide–ethanol solution. Collect the resin, wash with methanol, 1 *M* hydrochloric acid and water, then dry. The exchange capacity was found to be 0.39 mequiv./g by acid-base titration of the carboxylic acid.

RESULTS AND DISCUSSION

Preparation of resins

Resin I was prepared by reacting a porous, cross-linked polystyrene resin with succinic anhydride in a Friedel–Crafts reaction. The chemical structure of the derivatized resin can be written as $P–C_6H_4COCH_2CH_2CO_2H$ (P = polymer). Resin II was prepared by reacting the polystyrene resin with phenyl chloroformate in a Friedel–Crafts reaction, followed by hydrolysis to the carboxylic acid. The chemical structure can be written as $P–C_6H_4CO_2H$. Coppock [9] showed that phenyl chloroformate was required in the Friedel-Crafts reaction of aromatic hydrocarbons to obtain the expected aryl ester of the aromatic hydrocarbon. Alkylation of the hydrocarbon occurs with the use of alkyl chloroformates.

At first, resin I was prepared under very mild reaction conditions to give a carboxylic acid capacity <0.1 mequiv./g, which is within the range that is widely used for the sulfonic acid resins used in ion chromatography. However, this carboxylic acid resin failed to give any useful separations. Another batch of resin I was prepared under different reaction conditions to give a resin of much higher carboxylic acid capacity (0.60 mequiv./g). This resin (and others of similar capacity) was used very successfully for ion chromatographic separations.

Optimization of separation conditions

Earlier work with columns of sulfonated polymeric resins demonstrated that good separation of several divalent metal ions could be obtained using weakly complexing eluents of ethylenediammonium tartrate [1,2]. Almost all of the present work was done with carboxylic acid resin I. Separations of several divalent metal ions were obtained using eluents containing the ethylenediammonium 2+ cation and one or two of the following complexing anions: citrate, pyridine-2,6-dicarboxylate (PDA), oxalate, hydroxybutyrate and tartrate. The first three of these were found to give the best separations. The ethylenediammonium 2+ cation acts as a "pusher" to move the divalent metal ions down the column. The complexing anions act as "pullers" to aid the separation of metal ions based on the formation constant of each metal ion with that particular anion.

Experiments designed to optimize separation conditions showed that the ethylenediammonium cation and a complexing anion were both needed in the eluent. Broad peaks and few separations were obtained using the ethylenediammonium cation with only a non-complexing anion. Addition of any of the complexing anions tightened the chromatographic peaks considerably. However, very poor separations were obtained when the eluent contained a complexing anion in conjunction with a monovalent cation such as sodium. The presence of ethylenediammonium, or some other divalent cation, seemed to be necessary. Using an eluent consisting of ethylenediammonium and any of the mentioned complexing anions, there is a noticeable later eluting system peak at lower pH values (pH 4.0 to 4.8). The retention time of this system peak is well beyond that of any of the metal ions in a mixture and adds no interference. The majority of work reported here was at pH 5.0 and higher where the system peak is no longer noticed and can be ignored. The system peak never appeared in later chromatograms when doing successive injections.

The effect of varying pH was investigated using the ethylenediammonium oxalate eluents. The results in Table I show the logarithm of adjusted retention time to be a linear function of pH (t'_R increasing as the pH assumes a higher value). The metal ions studied fell into two distinct groups, one with a slope very close to 0.5 and the other with a slope of approximately 1.0. We have no explanation for these differences in slope except that some of the metal ions might form metal hydrogen oxalate complexes and the others simple metal oxalate complexes.

The pH study was conducted in the pH range where oxalate was predominantly in the 2− form. A complexing anion of a weaker acid would be converted more completely to the fully deprotonated forms as the pH is increased. This would increase its chelating ability and could therefore lead to lower t'_R values with increased pH.

TABLE I

LINEAR REGRESSION DATA FOR PLOTS OF LOG t'_R (ADJUSTED RETENTION TIME) *VS.* pH USING AN ETHYLENEDIAMMONIUM OXALATE ELUENT

Metal ion	pH range	Slope	Intercept	Correlation coef.
Ni^{2+}	5.4–6.8	1.03	−5.80	0.9994
Co^{2+}	5.0–6.8	0.50	−2.74	0.9822
Zn^{2+}	5.0–6.4	1.07	−5.80	0.9944
Fe^{2+}	5.4–6.8	0.53	−2.75	0.9802
Pb^{2+}	4.0–5.4	0.98	−4.06	0.9948
Cu^{2+}	4.2–5.8	0.97	−4.88	0.9952
Cd^{2+}	4.0–5.6	0.87	−3.52	0.9976
Mn^{2+}	4.2–7.2	0.52	−2.31	0.9986
Mg^{2+}	4.0–7.2	0.50	−2.10	0.9991
Ca^{2+}	4.0–7.2	0.50	−1.89	0.9962
Sr^{2+}	4.0–7.2	0.51	−1.86	0.9977
Ba^{2+}	4.0–7.2	0.51	−1.76	0.9980

Increasing the concentration of complexing anion in the eluent leads to more complete complexation of metal ions and thus to lower t'_R values. The value of t'_R for any given metal ion seems to be determined primarily by the formation constant of the metal–anion complex, although this is modified by the affinity of the resin for the uncomplexed metal cation. The importance of metal-anion formation constants is demonstrated by the PDA anion. PDA has a rigid planar structure which forms very strong complexes with transition metals leading to fast chromatographic elution. Alkaline earths, however, form weaker complexes allowing excellent chromatographic separation. The order of elution of metal ions for all complexing anions studied was found to be that of decreasing complex formation constants (see Table II).

An earlier study [1] with complexing eluents in conjunction with sulfonated resins showed that log t'_R is inversely proportional to log α_M, where α_M is the concentration ratio of free metal cation to the total metal cation in solution. This paper [1] also showed that log t'_R is a linear function of the logarithm of the ethylenediammonium concentration in the eluent.

Citrate systems

An eluent containing 1.0 m*M* ethylenediammonium ion and slightly lower concentrations of citrate

TABLE II

LOGARITHMS OF FORMATION CONSTANTS OF SELECTED METAL COMPLEXES

Reagent	Log formation constant								
	Cu^{2+}	Ni^{2+}	Co^{2+}	Zn^{2+}	Mn^{2+}	Mg	Ca^{2+}	Sr^{2+}	Ba^{2+}
Citric acid	5.60	5.11	4.83	4.70	3.70	3.25	3.18	2.81	2.55
PDA	8.80	6.60	6.35	6.43	4.70	2.02	4.30	3.50	3.13
Oxalic acid	4.53	3.70	3.25	3.43	2.60	2.10	1.66	1.25	1.02

at pH 5.4 was found to give some useful separations. Keeping the ethylenediammonium concentration and the pH constant, the citrate concentration of the eluent was varied from 0.2 to 0.6 m*M* in 0.1 m*M* increments. Poor separations were obtained at 0.2 m*M* and 0.6 m*M* citrate; the best separation was obtained at 0.3 m*M* citrate.

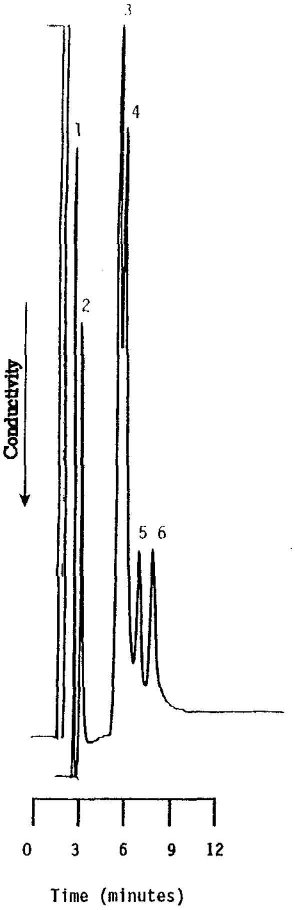

Fig. 1. Chromatographic separation on succinic acid-derivatized PS–DVB resin (resin I) column (50 × 4.6 mm I.D.). Eluent conditions: 1.0 m*M* ethylenediammonium, 0.30 m*M* citrate (pH 5.4). Peaks: 1 = Co^{2+}; 2 = Zn^{2+}; 3 = Mg^{2+}; 4 = Ca^{2+}; 5 = Sr^{2+}; 6 = Ba^{2+}.

Fig. 1 shows the separation of several metal ions at 0.3 m*M* citrate. The Ni^{2+} peak is covered by the injection peak. The Co^{2+} and Zn^{2+} peaks are well resolved even though the ratio of the logarithmic citrate formation constants is only 1.03 (Table II). The Ca^{2+} and Sr^{2+} peaks (ratio of log consants = 1.13) and Sr^{2+} and Ba^{2+} peaks (ratio of log constants = 1.10) are resolved but the resolution of the Mg^{2+} and Ca^{2+} peaks is poor, probably due to the very small ratio of their logarithmic formation constants (= 1.02).

Oxalate systems

Preliminary experiments showed that good separations of several metal ions could be obtained with an eluent containing 1.0 m*M* ethylenediammonium ion and 1.0 m*M* oxalate. The separation of Ni^{2+} (or Co^{2+}), Zn^{2+}, Mn^{2+}, Mg^{2+}, Ca^{2+} and Ba^{2+} was then optimized with respect to pH. Virtually no separation was obtained at pH 4.0 to 4.2 and the system peak was close to the metal ion peaks. By pH 4.4 some separation had begun and the system peak was well removed from the vicinity of metal ion peaks. The best separation occured around pH 5.3 with all six peaks being well separated (Fig. 2). Further increases in pH brought longer retention times, and by pH 5.8 the quality of the separation had deteriorated noticeably. At pH 6.4 almost no separation was obtained.

The metal ion retention times were next reduced by increasing the oxalate concentration from 1.0 m*M* to 1.6 m*M*. With this eluent, the optimum pH was approximately 5.8. It was possible to separate all seven metal ions in a mixture as shown in Fig. 3.

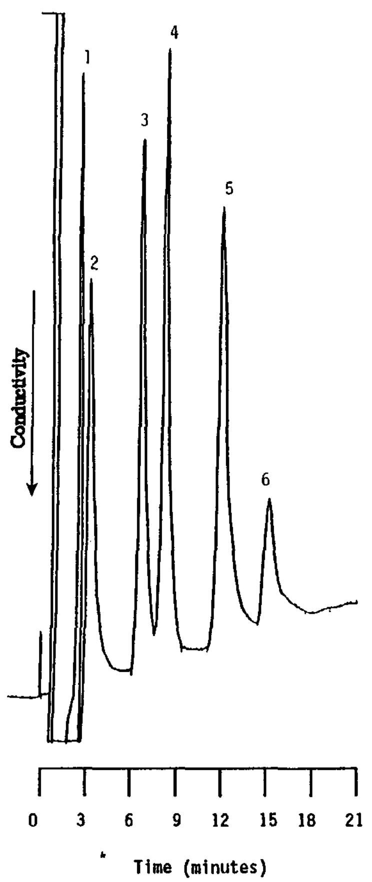

Fig. 2. Chromatographic separation on resin I column (100 × 4.6 mm I.D.). Eluent conditions: 1.0 mM ethylenediammonium, 1.00 mM oxalate (pH 5.3). Peaks: 1 = Co^{2+}; 2 = Zn^{2+}; 3 = Mn^{2+}; 4 = Mg^{2+}; 5 = Ca^{2+}; 6 = Ba^{2+}.

The use of resin II was next investigated. A short series of optimization experiments suggested the following conditions for separation: 0.75 mM ethylenediammonium, 1.5 mM oxalate and pH 4.5 to 5.0. Fig. 4 shows an excellent and rapid separation of Zn^{2+}, Mn^{2+}, Mg^{2+}, Ca^{2+} and Ba^{2+}. Ni^{2+} was partially separated from the Zn^{2+} peak.

These separations are similar to those obtained in Fig. 3 using resin I except for the pH which is lower for the separations using resin II. Based on the acid dissociation constants for the monomers of similar chemical structure, the acid strength of the carboxylic acid should be somewhat stronger for resin II. Except for this, we could not discern any major differences in the two resins for chromatographic separations.

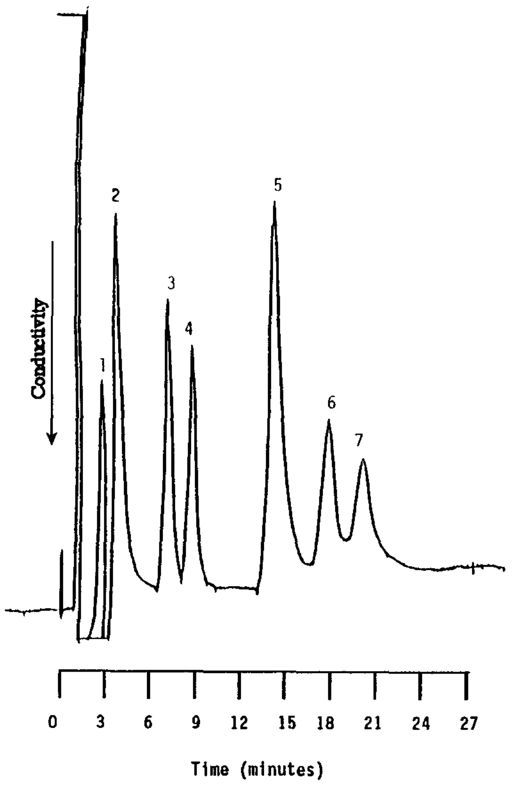

Fig. 3. Chromatographic separation on resin I column (100 × 4.6 mm I.D.). Eluent conditions: 1.0 mM ethylenediammonium, 1.60 mM oxalate (pH 5.8). Peaks: 1 = Co^{2+}; 2 = Zn^{2+}; 3 = Mn^{2+}; 4 = Mg^{2+}; 5 = Ca^{2+}; 6 = Sr^{2+}; 7 = Ba^{2+}.

PDA systems

PDA forms more stable complexes with most elements than oxalate or citrate. There is a reasonable difference in the formation constants of the PDA complexes listed in Table I. Preliminary optimization experiments showed that an excellent separation of Mg^{2+} and the three alkaline earths could be obtained with an eluent containing 1.0 mM ethylenediammonium and 0.05 or 0.1 mM PDA, adjusted to pH 5.4 (see Fig. 5). The order of elution is unusual in that Mg^{2+} elutes after the alkaline earths. In other chromatographic systems, Mg^{2+} elutes before Ca^{2+}. Increasing the PDA concentration in steps from 0.025 mM to 0.02 mM decreases the retention times of Ca^{2+}, Sr^{2+} and Ba^{2+} but has little effect on the retention time of Mg^{2+}. This effect was explained following theoretical considerations in earlier work by Sevenich and Fritz [1] in

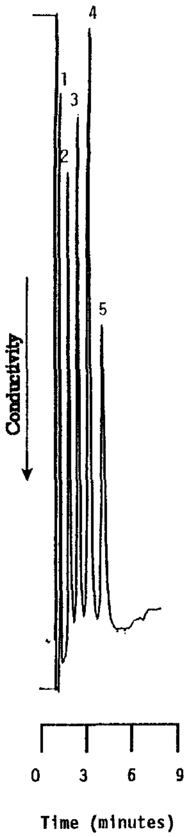

Fig. 4. Chromatographic separation on benzoic acid-derivatized PS–DVB resin (resin II) column (100 × 4.6 mm I.D.). Eluent conditions: 0.75 m*M* ethylenediammonium, 1.5 m*M* oxalate (pH 4.5). Peaks: 1 = Zn^{2+}; 2 = Mn^{2+}; 3 = Mg^{2+}; 4 = Ca^{2+}; 5 = Ba^{2+}.

which a similar ethylenediammonium tartrate eluent was used. They derived a logarithmic equation relating adjusted retention time to the fraction of the metal ion in solution that exists as the free metal cation (α_M). The equation was tested for a number of cations and linear plots were obtained when the concentration of the complexing anion in the eluent was varied and log t'_R was plotted against log α_M. In the present work using an ethylenediammonium–PDA eluent, when the concentration of PDA was increased from 0.025 to 0.200 m*M*, the following changes in α_M values were calculated: Ca^{2+} (0.495 to 0.095); Sr^{2+} (0.863 to 0.438); Ba^{2+} (0.937 to 0.649); Mg^{2+} (0.995 to 0.860). Linear plots were obtained for Ca^{2+}, Sr^{2+} and Ba^{2+} when plotting log t'_R against log α_M. In each case the value of α_M decreased by 30–40% for the increased PDA concentration. Mg^{2+}, however, showed only a 3.5% decrease in α_M for the same increase in PDA concentration. This very weak complexation of Mg^{2+} by the PDA accounted for the negligible effect on the retention time of Mg^{2+}.

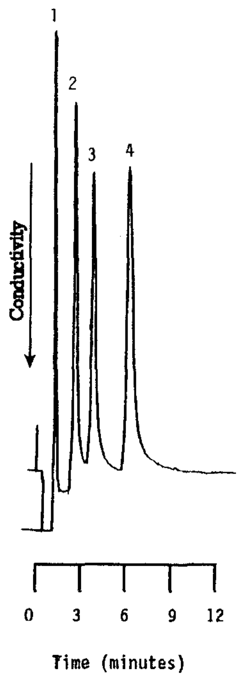

Fig. 5. Chromatographic separation on resin I column (50 × 4.6 mm I.D.). Eluent conditions: 1.0 m*M* ethylenediammonium, 0.10 m*M* PDA (pH 5.4). Peaks: 1 = Ca^{2+}; 2 = Sr^{2+}; 3 = Ba^{2+}; 4 = Mg^{2+}.

Using a longer column than that used to obtain Fig. 5, the retention times of Ca^{2+}, Sr^{2+}, Ba^{2+} and Mg^{2+} are somewhat increased allowing separation of some additional early-eluting ions. Fig. 6 shows an excellent separation of Zn^{2+}, Na^+, Ca^{2+}, Sr^{2+}, Ba^{2+} and Mg^{2+} at pH 5.4 on a 10-cm column. Very similar chromatograms were obtained for samples in which Co^{2+} or Cu^{2+} was substituted for Zn^{2+} and K^+ or NH_4^+ was present instead of Na^+. The same desired effect was achieved by increasing the pH from 5.4 to 5.8 using the shorter column. An equally good and somewhat faster separation was obtained at pH 5.8 on a 5-cm column.

Linear calibration curves were obtained for the ions separated by plotting peak area *vs.* concentra-

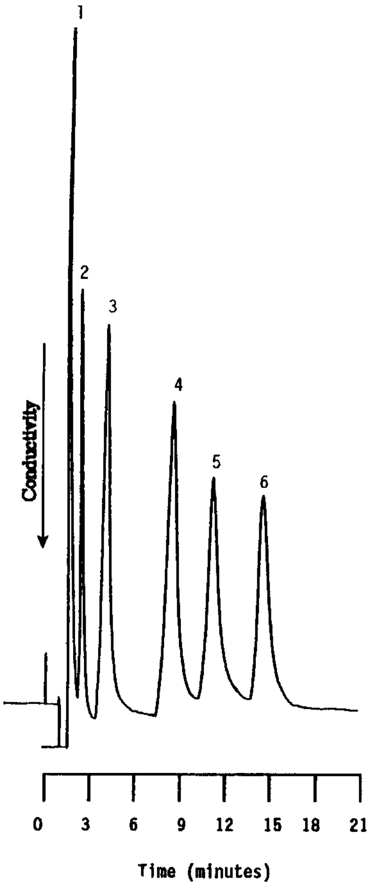

Fig. 6. Chromatographic separation on resin I column (100 × 4.6 mm I.D.). Eluent conditions: 1.0 m*M* ethylenediammonium, 0.05 m*M* PDA (pH 5.4). Peaks: 1 = Zn^{2+}; 2 = Na^+; 3 = Ca^{2+}; 4 = Sr^{2+}; 5 = Ba^{2+}; 6 = Mg^{2+}.

tion. The curves remained linear over the studied concentration range of 10^{-4} to 10^{-2} *M*. The desirable goal of separating an alkali metal from several divalent metal ions in a single run has thus been achieved. Unfortunately, we were not able to separate Na^+, K^+ and NH_4^+ from one another. The sum of these monovalent ions can be obtained but this would be difficult to quantify because of the differing responses of the conductivity detector for these ions. A dicarboxylic derivatized resin could possibly accomplish this task.

ACKNOWLEDGEMENTS

We wish to thank Doug Gjerde of Sarasep Inc. for the gift of porous polymeric resins used to prepare the carboxylic acid resins used in this work.

Ames Laboratory is operated for the US Department of Energy under Contract No. W-7405-Eng-82. This work was supported by the Director of Energy Research, Office of Basic Energy Sciences.

REFERENCES

1 G. J. Sevenich and J. S. Fritz, *Anal. Chem.*, 55 (1983) 12.
2 G. J. Sevenich and J. S. Fritz, *J. Chromatogr.*, 347 (1985) 147.
3 H. Saitoh and K. Oikawa, *J. Chromatogr.*, 329 (1985) 247.
4 H. Sato, *Bunseki Kagaku*, 34 (1985) 606.
5 B. Kondratjonok and G. Schwedt, *Fresenius' Z. Anal. Chem.*, 332 (1988) 333.
6 D. Yan and G. Schwedt, *Fresenius' Z. Anal. Chem.*, 320 (1985) 325.
7 S. Reiffenstuhl and G. Bonn, *Fresenius' Z. Anal. Chem.*, 332 (1988) 130.
8 P. Kolla, G. Schomburg and M. W. Laubli, *Chromatographia*, 23 (1987) 465.
9 W. Coppock, *J. Org. Chem.*, 22 (1957) 325.