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ANION–CATION SEPARATIONS ON A MIXED BED ALUMINA–SILICA COLUMN

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SUMMARY

Mixed bed ion-exchange (MBIE) columns containing alumina and silica were evaluated for the simultaneous separation of anion and cation analytes. At the mobile phase pH used alumina provides anion exchange sites while silica provides cation exchange sites. Since alumina and silica exhibit weak acid and base properties, their anion and/or cation exchange properties are pH dependent. Ion exchange capacities, rates of exchange and analyte ion exchange selectivities are also pH dependent. The major mobile phase parameters affecting analyte anion and cation resolution and elution order are pH and type and concentration of counter anion and counter cation, respectively. The weight ratio of the two exchangers and/or the exchange capacities of the two in the column can also be used to alter resolution and elution order. Several examples of the simultaneous separation of inorganic mono- and divalent anions and cations using a single sample injection, a single column and a single detector (conductivity) illustrate the parameters and scope of the alumina–silica MBIE column.

INTRODUCTION

A mixed bed column of ion exchangers is the incorporation of both cation and anion exchanger particles interspersed throughout the same column. Historically, these kinds of columns have been used as an alternative to a two stage or multistage approach where anion and cation columns are connected in series for the removal of electrolytes from water in water treatment processes.

Applications of mixed beds of anion and cation exchangers (hereafter referred to as MBIE columns) to analytical separations has been limited. MBIE columns were used to separate alkaline earths, transition metals and rare earth^{1–5} from mobile phases containing ligands that converted metal ions into anionic complexes. Subsequent work suggested that the separations were often not improved over the sole use of either an anion or cation exchanger⁶. MBIE silica based columns^{7,8} containing phenyl modified silica were used for the separation of acidic and basic proteins while polymer based MBIE columns were used for the simultaneous separation of inorganic anions and cations⁹. The latter study also demonstrated that the column and mobile phase parameters affecting retention, selectivity and resolution are typical of conventional anion and cation exchange.

Other chromatographic strategies other than MBIE columns have been used for the simultaneous separation of anions and cations. Dual anion and cation columns with a single conductivity detection with synchronal sample injection¹⁰ and anion and cation columns connected in series with indirect photometric detection^{11,12} have been used. In another approach a single sample, anion and cation column in series, and two detectors were used¹³⁻¹⁵. It is also possible to use a ligand in the mobile phase which converts metal ions into anionic complexes. These are separated on an anion exchanger along with other anions present in the sample^{16,17}. Column switching techniques have also been described^{18,19}.

The ion exchange properties of inorganic oxides have been recognized for a long time²⁰. Recent studies with modern, spherical alumina^{21,22} and silica^{23,24} microparticles have shown that these oxides can function as efficient stationary phase ion exchangers for liquid chromatographic anion and cation exchange separations, respectively. Exchange rates, exchange capacities and ion selectivities for these microparticles^{22,24} were found to be vastly improved over the characteristics reported for the classical, irregular shaped alumina and silica macroparticles²⁰. Unlike polymeric derived strong acid or base ion exchangers, oxides are generally weak acid or base ion exchangers and pH plays a major role in determining the oxide's exchange capacity, ion selectivity and its ability to act as an anion or cation exchanger since many oxides exhibit amphoteric behavior.

This report focuses on using a MBIE column composed of alumina and silica microparticles. Because of the mobile phase pH, alumina provides anion exchange sites while silica provides cation exchange sites. Thus, it is possible to efficiently separate anions and cations simultaneously by using one alumina-silica MBIE column with a single sample injection, one eluent and one detector while maintaining the unique analyte ion selectivities provided by alumina and silica.

EXPERIMENTAL

Reagents

Inorganic salts used as electrolytes and buffers in the mobile phase and as analytes were analytical reagent grade when possible. LC water was obtained by passing distilled water through a Sybron/Barnstead water purification unit. Bulk form, spherical alumina (5 and 10 μm , Spherisorb A5Y and A10Y from Phase Separations) and silica (6 μm , Zorbax silica from DuPont) were used in stainless-steel 150 mm \times 4.1 mm I.D. columns.

Instrumentation

A Varian M2010 pump, Waters U6K injector and Waters M430 conductivity detector were used. Column temperature was maintained at 35°C by circulated water from a constant temperature bath. Peak area was determined with a Spectra Physics M4100 Integrator.

Procedures

Weighed quantities of alumina and silica were added to 20 ml of a solution that contained 100 g sodium chloride per liter of LC water. The slurry mixture was carefully stirred in a column packing reservoir for 10 min. Columns were packed upward using

a procedure outlined elsewhere²². To ensure hydration of the alumina and silica, newly packed columns were conditioned overnight with an aqueous 2.5 mM lithium acetate mobile phase. In general, columns were conditioned for several hours at 1 ml/min when switching from one mobile phase to another. Typical column efficiencies were 8000 plates/meter for Na⁺ and 25 000 plates/meter for Cl⁻ using an aqueous pH 5.03, 2.50 mM lithium acetate mobile phase. All newly prepared columns and periodic testing of columns used during the studies were compared to these efficiency standards. Inlet column pressure at 1 ml/min was typically 500 to 900 p.s.i. Analyte solutions were prepared by dissolving weighed amounts of salt in water at about 1 mg/ml in glass vials. Sample aliquots delivered by 10- μ l syringe were 1–10 μ l. Aqueous mobile phases were prepared by titrating standard acetic acid solution with a standard lithium hydroxide solution to the desired pH followed by dilution to volume.

RESULTS AND DISCUSSION

As mobile phase pH is changed from acidic to basic the surface charge on silica and alumina changes from positive to negative, respectively. This transition point or isoelectric point pH is dependent on the chemical environment and the conditions used for the oxide preparation^{20–26}. Depending on the buffer components the isoelectric point pH for silica is about 2 while for alumina the value varies between 3.5 to 9.2. Silica does not exhibit a useful amphoteric behavior because of its reactivity in acidic solutions. Thus, in column experiments only its cation exchange behavior above approximately pH 2 is useful. Alumina in contrast is capable of exhibiting both anion (low pH) and cation (high pH) exchange because of its chemical stability in both environments. Since the two oxides exhibit weak acid and base characteristics, the available and useful exchange capacities of the two oxides are also pH dependent. Under favorable pH conditions and in the presence of suitable buffer components cation exchange capacity on silica and anion exchange capacity on alumina can approach about 3.5 and 4 mequiv./g, respectively²⁵.

When the two oxides are intimately mixed in an aqueous solution and the pH is adjusted between 2 and 8, silica is a cation exchanger and alumina is an anion exchanger. As the pH is increased cation exchange capacity for silica increases and anion exchange capacity for alumina decreases while at the lower pH the reverse occurs. Adjustment of pH within this approximate pH range alters the two exchange capacities and as either of the two extremes are approached a sufficient number of exchange sites for the lesser one is still present for modern ion-exchange chromatography. Since the isoelectric point pH is also dependent on the buffer components^{20–26}, exchange capacity at a given pH is also dependent on the type of buffer components and their concentration.

A second important ion exchange characteristic of oxides is that the exchange selectivities often differ not only from oxide to oxide but also when compared to polymeric based strong acid and base ion exchangers. For example, alkali metal and alkaline earth retention order on silica at cation exchange conditions is identical to that on a sulfonated styrene based cation exchanger. In contrast anion retention order on alumina under anion exchange conditions is significantly different than with quaternary ammonium styrene based anion exchangers. On alumina anion elution order is F⁻ > SO₄²⁻ > Cl⁻ > Br⁻ > I⁻ > ClO₄⁻ while for the styrene based anion exchanger it is SO₄²⁻, ClO₄⁻ > I⁻ > Br⁻ > Cl⁻ > F⁻ (ref. 22).

Mixed bed column performance

High pressure packing of a well stirred slurry mixture of the two oxides provided a uniformly interspersed packed column. Reproducible chromatographic data were obtained from a series of identically packed columns and visual examination of the packing when it was purposely extruded from a packed column supported this conclusion. Initial column experiments using several different salts as sources of cation and anion analytes indicated a favorable column performance and that anions and cations could be efficiently separated and detected by conductivity.

A 2.5 mM acetic acid, 1.85 mM lithium hydroxide, pH 5.03 aqueous mobile phase, a 150 mm × 4.1 mm column packed with alumina and silica at a 1:1 ratio and KI as an analyte were used to evaluate column performance. When the flow-rate was increased by 0.5-ml/min increments up to 2.0 ml/min, capacity factor, k' , values for K^+ retention decreased from 3.02 (0.5 ml/min) to 2.53 (2.0 ml/min) while for I^- , k' values were constant at 7.25. Plates/m for K^+ changed from 2800 to 2760 while for I^- the change was from 24 300 to 18 700 plates/m. Change in peak symmetry was insignificant. At 1.0 ml/min column inlet pressure was about 600 p.s.i. Using a constant injected sample volume of 1 μ l the k' value for K^+ and I^- remained constant as the amount of KI injected increased from 0.1 to 8 μ g. Similarly, when using a sample that was 0.6 μ g of KI/ μ l, no change in k' was observed as the sample volume was increased from 2 to 30 μ l. Thus, neither a mass or volume overload was indicated over the range of conditions studied suggesting that linear anion and cation ion exchange isotherms are present. Since anion and cation exchange capacity for alumina and silica, respectively, are pH dependent the mass and volume overload condition will also depend on the pH. At pH 5.03, which was used in most of these experiments, anion and cation exchange capacities for alumina and silica are about 0.5 and 0.1 mequiv./g, respectively; no attempt was made to accurately determine the exchange capacities at the experimental conditions used. When the ratio of alumina to silica was changed retention times of analyte anions and cations changed accordingly. If alumina was in excess anion retention increased and cation retention decreased while if silica was in excess the reverse effect was observed. In experiments reported here 1:1 alumina:silica was used.

Conductivity detection was used in all experiments reported here. Thus, selection of mobile phase counter cations and counter anions affects not only the ion exchange equilibria as a result of ion exchange selectivity, but also detection because of differences in equivalent ionic conductances between counter ions and analyte ions. Lithium acetate provides suitable counter anion and cation ion exchange selectivities and equivalent conductances and was used as the mobile phase electrolyte in most of the experiments described here.

Peak identification was achieved by using combinations of different salts as analytes. For example, alkali metal and halide peaks were identified by recording and comparing the chromatograms obtained for each alkali metal halide salt as an analyte. When combined with chromatograms obtained with other salts as analytes peak assignment is further supported.

pH

Mobile phase pH determines the ion exchange capacity of alumina and silica. As pH increases, cation exchange capacity of silica increases while the anion exchange

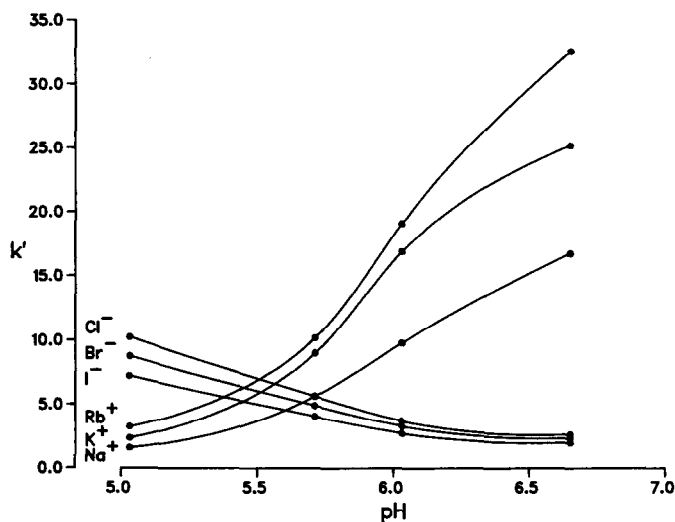


Fig. 1. Effect of mobile phase pH on analyte ion retention. The aqueous mobile phase is 2.50 mM acetic acid solution containing 1.85, 2.31, 2.39 or 4.90 mM LiOH at 1.0 ml/min and 35.0°C.

capacity of alumina decreases. The reverse occurs as pH is lowered. Since analyte ion retention time is influenced by exchange capacity, it must therefore also be influenced by pH. A high mobile phase pH should cause analyte cation retention to increase and analyte anion retention to decrease. The reverse should occur as pH is lowered. Fig. 1 illustrates these trends, where retention expressed as k' is plotted as a function of mobile phase pH using alkali metal halide salts as the analytes. The effect of pH on retention is significant and over a 2 pH unit change from pH 5 to 7 the alkali metal cation and halide anion retention is reversed. As shown in Fig. 2 as little as a 1.5 pH shift in the mobile phase is sufficient enough to reverse the elution order of cations and

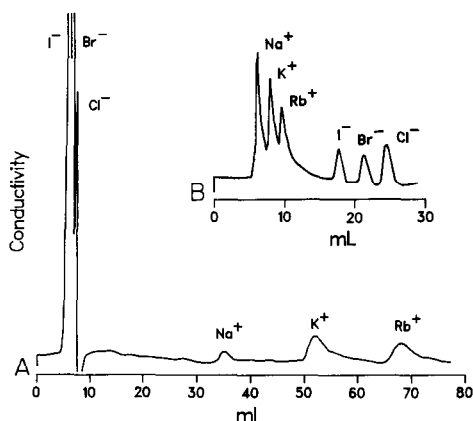


Fig. 2. Simultaneous separation of monovalent cations and anions on a 1:1 alumina:silica column as a function of pH. The aqueous mobile phases are (A) 2.50 mM acetic acid, 4.90 mM LiOH at pH 6.65 and (B) 2.50 mM acetic acid, 1.90 mM LiOH, pH 5.03 at 1.0 ml/min and 35.0°C.

anions. Figs. 1 and 2 also demonstrate that the anion elution order for the alumina-silica MBIE column is characteristic of alumina functioning as an anion exchanger²² and the cation order is characteristic of silica functioning as a cation exchanger²⁴.

Mobile phase ionic strength

Increasing the mobile phase counter cation and anion concentration will decrease analyte cation and anion retention, respectively, which is consistent with an ion exchange process. This effect is illustrated in Fig. 3 where analyte anion and cation retention is plotted as a function of mobile phase ionic strength using lithium acetate as the ionic strength salt. If a counter cation of higher ion exchange selectivity is used analyte cation retention is lowered. Similarly using a counter anion of higher ion exchange selectivity lowers analyte anion retention. When lithium acetate was used (see Fig. 3) the effect of increasing acetate concentration on decreasing analyte anion retention is larger than the effect of increasing Li^+ concentration on decreasing analyte cation retention. Several reasons contribute to this observation. (1) Acetate exchange selectivity towards anions is more favorable than Li^+ selectivity toward cations. (2) Increasing acetate concentration reduces the isoelectric point pH which lowers the anion exchange capacity of alumina^{21,22,23} and thus analyte anion retention is reduced.

Fig. 4 illustrates how an increase in mobile phase counter ion concentration can alter elution order. Two major effects can be realized. (1) Increasing electrolyte concentration automatically decreases both analyte anion and cation retention since both counter cation and anion concentration must increase. (2) Because ion exchange selectivities are unique it is possible, for example, to select a mobile phase salt that provides a counter cation that causes retention of analyte cations to be reduced to

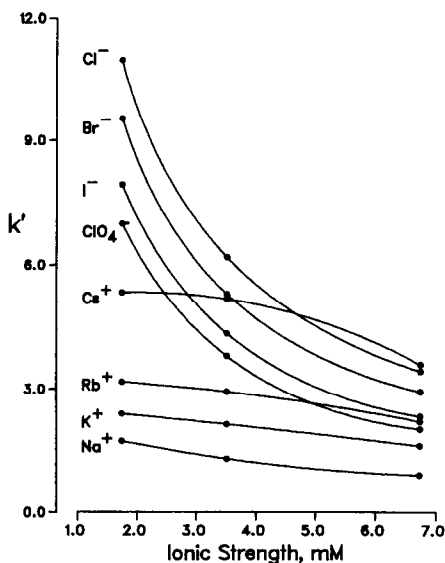


Fig. 3. Effect of mobile phase ionic strength on analyte ion retention. The aqueous mobile phases are lithium acetate pH 5.0, at 1.0 ml/min and 35.0°C.

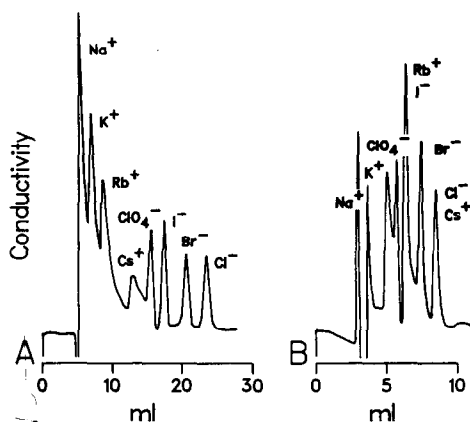


Fig. 4. Effect of mobile phase ionic strength on the separation of monovalent cations and anions on a 1:1 alumina:silica column. The aqueous mobile phases are (A) 2.50 mM acetic acid, 1.85 mM LiOH, pH 5.01 and (B) 10.0 mM acetic acid, 7.00 mM LiOH, pH 5.00 at 1.0 ml/min and 35.0°C.

a greater extent than the affect of the counter anion on analyte anion retention. Alternatively, a salt can be chosen, as in Fig. 4, that provides a counter anion that has a more significant affect on anion retention than the counter cations effect on cation retention.

Calibration graph

Calibration graph reproducibility for the simultaneous separation and determination of anions and cations on the alumina-silica MBIE column was evaluated using NaCl and CaCl₂ as analytes. A Micrometrics M725 autoinjector (sample injection 20 μ l) was used in these experiments. For NaCl the aqueous mobile phase was 2.50 mM acetic acid, 1.85 mM LiOH, pH 5.03, while for CaCl₂ it was 10.0 mM acetic acid, 7.13 mM KOH, pH 5.02. The column was 150 mm \times 4.1 mm, alumina-silica. A stronger eluent (increased counter ion concentration and K⁺ which has a higher cation exchange selectivity compared to Li⁺) was used for the CaCl₂ analyte because of the higher retention of Ca²⁺.

For NaCl the calibration graph was linear from 0.50 to 254 μ g NaCl per 20- μ l injection; no attempt was made to determine the upper limit of linearity. For Na⁺ the calibration graph corresponded to: peak area (10^7) = 3.679 (ng Na⁺) (10^4) + 0.02254 with a correlation coefficient of 0.9979, while for Cl⁻ it was peak area (10^7) = 0.9844 (ng Cl⁻) (10^4) - 0.006334 with a correlation coefficient of 0.9999. The detection limits at the mobile phase-detector conditions used were 0.5 and 0.03 μ g per 20 μ l injection for Na⁺ and Cl⁻, respectively. For CaCl₂, which was studied over the range of 0.45 to 90.7 μ g of CaCl₂ per 20 μ l injection, linear calibration graphs for Ca²⁺ and Cl⁻ were: peak area (10^6) = 0.7790 (ng Ca²⁺) (10^3) + 0.2459 with a correlation coefficient of 0.9994 and peak area (10^6) = 0.5323 (ng Cl⁻) (10^4) - 0.005676 with a correlation coefficient of 0.9998, respectively. Detection limits for the experimental conditions used were 0.100 μ g Ca²⁺ and 0.071 μ g Cl⁻ per 20- μ l injection, respectively. For both NaCl and CaCl₂ as analytes retention times for Na⁺ and Cl⁻ and Ca²⁺ and Cl⁻ were constant over the range of NaCl and CaCl₂ injected.

Separations

The alumina-silica MBIE column performance is favorable, reliable and the column is applicable to the separation of a variety of mono- and divalent anion and cation analyte ions. Under favorable conditions peak shapes are well defined and column efficiencies, which are typical of polymeric exchangers particularly anion exchangers, approach 8000 and 25 000 plates per meter for cations and anions, respectively. Manipulation of the alumina to silica ratio, pH, eluent counter ions and their concentration are the major factors used to improve resolution and/or to shift retention order of anion analytes relative to cation analytes and *vice versa*. Analyte retention times were reproducible providing the mobile phase pH was maintained within the pH stability range of alumina and silica. Certain eluent counter ions should be avoided when using alumina²² and silica²⁴ because they can cause column plugging due to particle breakdown and/or change the exchange sites due to chemical reaction. This is particularly true of alumina where F^- and multivalent anions cause a permanent change in alumina's performance as an anion exchanger. The effect of F^- is rapid with a permanent loss in anion exchange capacity while, in general, multivalent counter anion effects are more gradual and often only reduce exchange capacity. Counter ions that exhibit ligand characteristics toward Al and/or Si should also be avoided.

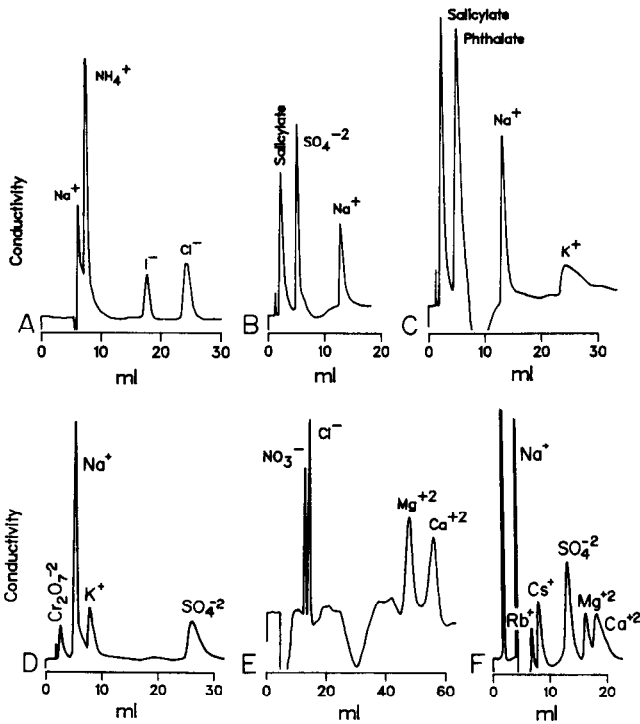


Fig. 5. Simultaneous separation of cations and anions on a 1:1 alumina:silica column. The aqueous mobile phases are (A) 2.50 *M* acetic acid, 1.85 *M* LiOH, pH 5.03, (B) and (C) 2.00 *M* H_3PO_4 , 2.00 *M* LiOH, pH 4.75, (D) 2.00 *M* H_3PO_4 , 1.90 *M* LiOH, pH 3.97, (E) 5.00 *M* acetic acid, 3.60 *M* KOH, pH 5.03, (F) 4.00 *M* H_3PO_4 , 3.90 *M* KOH, 2.00 *M* KCl, pH 3.93 at 1.00 ml/min and 35.0°C.

Several examples of mono- and divalent anion and cation separations are illustrated in Fig. 5. In all cases a 150 mm \times 4.1 mm, 1:1 alumina-silica MBIE column and conductivity detection was used. In general, salts used as analytes were first injected individually at about 1 μ g or less in 1 to 10 μ l volumes to establish cation-anion retention. Figs. 2, 4 and 5A demonstrate that monovalent anions and cations are easily separated using an aqueous lithium acetate mobile phase at about pH 5. If the mobile phase pH is increased anion retention decreases and cation retention increases; a pH decrease reverses the effect. These trends are due to the effect of pH on exchange capacity and the isoelectric point pH. Mobile phase pH will also affect analyte retention through its influence on analyte ionization. Thus, in Fig. 5A at pH 5.0 ammonia is retained and separated from Na⁺ as the cation. In Fig. 5A the injected sample contained 1.0 μ g of NaI and 0.74 μ g of NH₄Cl.

Divalent analyte ions are more retained than monovalent analyte ions. Thus, to maintain reasonable elution times, eluent strength must be increased. Fig. 5B, C and D illustrate separations of monovalent cations and highly retained anions. Eluent strength was increased by using a lithium phosphate mobile phase. Since pH is 4.75 (Fig. 5B, C) and 3.97 (Fig. 5D) the eluent counter anion is primarily an equilibrium mixture of H₂PO₄⁻/HPO₄²⁻ and this provides a much stronger eluent counter anion mixture than obtained with an acetate mobile phase. The change in pH between Fig. 5B, C and D is also a factor. At the higher pH (Fig. 5B, C) cation exchange capacity of silica is enhanced and anion exchange capacity of alumina is reduced while the lower pH (Fig. 5D) causes the reverse effect. This accounts for the significant difference in retention times for Na⁺, K⁺ and SO₄²⁻ between Fig. 5B, C and D. Fig. 5B and C also show that organic analyte anions can be effectively separated in an alumina-silica MBIE column. Since these are derived from weak acids and their ionization is pH dependent, their elution time is also affected by pH.

The selection of multivalent anions as mobile phase counter ions must be done carefully. Because of strong interactions between alumina or silica and multivalent anions and the resulting change in the oxide surface^{22,24-26} not all multivalent counter anions are useful as eluents. For example, when a 2.5 mM lithium acetate mobile phase is used Na⁺ retention is significantly lower (see Fig. 2B) than when the lithium phosphate mobile phase (see Fig. 5B and C) is used even though Li⁺ is the counter cation in the two mobile phases. A similar effect on anion elution was also observed. The slight difference in Li⁺ concentration does not account for this observation. The increase in retention is apparently the result of an irreversible change in the alumina-silica surface due to a phosphate interaction. Even after reconditioning the column with excessive quantities of 0.10 M NaCl mobile phase the original Na⁺ retention from a lithium acetate mobile phase could not be obtained. Other multivalent eluent counter anions or anions that complex with alumina and/or silica will also cause irreversible oxide surface change^{22,24}. Thus, while a phosphate mobile phase can be used to effectively and reproducibly elute more highly retained anions it does so by permanently changing the column. The change, however, does not eliminate preparation of reproducible peak shapes and calibration graphs (see calibration graph section).

Fig. 5E illustrates the separation of divalent cations from monovalent anions. In this case a potassium acetate mobile phase was used. The counter cation K⁺, which has a higher cation exchange selectivity relative to Li⁺, was used in the mobile phase; its

concentration relative to Li^+ was also increased in order to increase eluent strength. Fig. 5F illustrates a separation where both a strong eluent cation (K^+) and anion (phosphate buffer) are used effectively to separate highly retained cations and anions. Counter ion concentration was also increased to improve eluent strength and pH was lowered to decrease cation exchange capacity of silica and thus to reduce analyte cation retention.

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