The ion chromatographic separation of high valence metal cations using a neutral polystyrene resin dynamically modified with dipicolinic acid

James Cowan,* Matthew J. Shaw,† Eric P. Achterberg,* Phil Jones,*a and P. N. Nesterenko* b

a Department of Environmental Sciences, University of Plymouth, Plymouth, Devon, UK PL4 8AA. E-mail: pljones@plymouth.ac.uk
b Department of Chemistry, Lomonosov Moscow State University, Vorobyevy Gory, GSP-3, Moscow 119899, Russian Federation

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A neutral polystyrene resin column, dynamically loaded with dipicolinic acid at a concentration of 0.1 mm in 1 m potassium nitrate eluent, was investigated for the separation characteristics of a number of high valence metal cations over the pH range 0–3. The metal species studied were Th(IV), U(IV), Zr(IV), Hf(IV), Hi(IV), Ti(IV), Sn(IV), V(IV) and V(V), Fe(III) and Bi(III), of which Th(IV), Si(IV), V(IV) and Fe(III) did not show any retention. For the remaining metal ions, significant retention was obtained with good peak shapes, except for Th(IV), which moved only slightly from the solvent front with some tailing. The retention order at pH 0.3 was Th(IV)<V(IV)<Bi(III)<U(IV)<Hf(IV)<Zr(IV). A notable feature of this separation system was the high selectivity shown for uranium, zirconium and hafnium, the last two being nearly resolved in 15 min on the relatively short 10 cm column.

Introduction

The ion exchange separation of high valence metal ions has always posed a notable challenge, as special, sometimes extreme, elution conditions are necessary for their separation. In particular, those high valency metal ions with relatively slow reaction kinetics, which form cationic species in non-complexing acid media, are especially troublesome. These include Th(IV), U(IV) and U(III), Pu(III) and Pu(IV), Np(IV) and Np(V), Zr(IV), Hf(IV), Ti(IV), Sn(IV), V(IV) and V(V) and a number of trivalent ions such as Bi(III), Tl(III), Fe(III), Ru(III) and Rh(III). The main problem is that significant hydrolysis and polymerisation can occur unless the pH is quite low. These elements are always posed a notable challenge, as special, sometimes targeted to only two or three metal species.

Invariably, selectivity is a major problem and serious interference can occur, resulting from large amounts of species such as Fe(III) and the lanthanides in the sample. High salt content can also cause a problem where ion exchange sites can be swamped by the high ionic strength. Another important area involving high valency metal ions is the separation of V(V) from V(IV), of interest for the investigation of the biological role of vanadium. Most of the recent studies on the separation and determination of acid hydrolysing metals tend to develop methods specifically targeted to only two or three metal species. Inevitably, selectivity is a major problem and serious interference can occur, resulting from large amounts of species such as Fe(III) and the lanthanides in the sample. This high salt content can also cause a problem where ion exchange sites can be swamped by the high ionic strength. Another important area involving high valency metal ions is the separation of V(V) from V(IV), of interest for the investigation of the biological role of vanadium. Most of the recent studies on the separation and determination of acid hydrolysing metals tend to develop methods specifically targeted to only two or three metal species.

Many of the studies so far using high-performance chelation ion chromatography have involved the lower valence metal ions, such as the dipositive charged transition metals lead and cadmium, but little work has yet been published involving the separation of the more difficult acid hydrolysing metals.

Some of the studies of high valence metal ions by chelation ion chromatography have been carried out on chelating dye impregnated resins. Sutton et al. used neutral polystyrene resins impregnated with either calamine or 4-(2-pyridylazo)resorcinol, both azo dyes, to separate uranium from thorium. In a similar approach, Paull and Haddad impregnated a polystyrene resin with the chelating dye Methylene Blue (imidodiacetic acid functionality) to determine trace uranyl ion in saline samples. Chelating resins formed by dynamic loading have also been investigated. Sutton et al. found that dynamically loading a hypercrosslinked resin with dipicolinic acid resulted in the highly selective separation of uranium from thorium, lanthanides and Fe(III). Shaw et al. followed up this work and developed a dipicolinic acid dynamically loaded chelating column method for the determination of uranium in sediments. An interesting finding arising from this study was the
appearance of a later eluting peak subsequently identified as zirconium, which was known to be present in the sediment. The implication from this was that a dipicolinic acid loaded column showed potential for the high efficiency separation of a wider range of high valency metals species in complex samples and was thus worthy of further investigation.

The work in this paper describes a preliminary study of the chromatographic performance and retention characteristics of a number of acid hydrolysing metals on a high efficiency resin dynamically loaded with dipicolinic acid. The effect of temperature and pH changes on separation and selectivity are summarised together with selected examples of chromatograms of metal mixtures.

Experimental

Instrumentation

The isocratic ion chromatographic system consisted of a Dionex GP40 gradient pump (Dionex, Sunnyvale, CA, USA) and a Rheodyne 9010 polyether ether ketone (PEEK) liquid six port injection valve (Rheodyne, Cotati, CA, USA), fitted with a 100 μl PEEK sample loop. The analytical column was a PEEK (100 × 4.6 mm id) casing, packed with 5 μm PLRP-S polystyrene divinylbenzene resin (Polymer Laboratories, Shropshire, UK). The post-column detection system comprised a Dionex IP20 pump to deliver the post-column reagent (PCR), a zero dead volume PTFE tee and a 2 m × 0.5 mm id PTFE reaction coil.

Detection was achieved using a Shimadzu SPD-10AVvp UV–vis spectrophotometer (Shimadzu Corporation, Kyoto, Japan) set at 654 nm for Arsenazo III and 585 nm for pyrocatechol violet (PCV) post-column reagents.

Reagents

Two post-column reagents were used in this study, (i) A solution of 12 mg l⁻¹ Arsenazo III in 1 M HNO₃ was used for all the metals except V(IV) and V(V). (ii) A solution of 40 mg l⁻¹ PCV in 1.5 M hexamine was used for V(IV) and V(V).

The eluent consisted of a 1 M KNO₃ aqueous solution containing 0.1 mM dipicolinic acid and nitric acid of varying concentration, depending on the pH required. Both the eluent and PCR were delivered at 1 ml min⁻¹.

All reagents were of BDH AnalR grade (Merck, Poole, UK) with the exception of Arsenazo III (95% dye content) (ICN Biomedicals Inc., Aurora, OH, USA), dipicolinic acid (99% purity), PCV and titanium oxysulfate (Aldrich, Gillingham, Dorset, UK). 1000 mg l⁻¹ metal stock solutions of Th(IV), U(vi), Zr(IV), Sn(IV), Fe(in) and Bi(in) were obtained from Merck and Hf(IV) from Aldrich. A 1000 mg l⁻¹ stock solution of V(IV) was prepared from ammonium vanadate dissolved in 1 M nitric acid. V(IV) solutions were prepared from V(v) stock by adding excess solid sodium sulfite and standing for 5 min before use. An approximate 1000 mg l⁻¹ stock solution of Ti(v) was prepared by dissolving titanium oxysulfate in 1 M nitric acid. The metal solutions were diluted to working standards with deionised water (Milli-Q, Millipore, Milford, MA, USA), containing sufficient nitric acid to prevent hydrolysis, and stored in poly(propylene) bottles (Merck).

Results and discussion

Metals with high positive charge have a strong affinity for the oxygen in water molecules and tend to form hydroxy, oxo, and oxo-hydroxy species in aqueous media, even at low pH. It is beyond the scope of this short article to discuss this very complex area of inorganic chemistry in any detail. Any classification can be criticised, but the authors suggest that they can be essentially divided into two broad classes, those which form anions such as oxo anions at virtually all pHs, e.g. Cr(vi), Mn(vii), Mo(vi) and W(vi), and those which form cationic species at low pH. This work concerns a number of the metals from the latter group, namely, Th(IV), U(vi), Zr(IV), Hf(IV), Ti(IV), Sn(IV), V(IV), V(V), Bi(in) and Fe(in). For the sake of simplicity they will be called the acid hydrolysing group. Many of these cations will contain oxo and hydroxy groups and as the exact nature of many of the aqua cations is not known, the metal species will be designated simply by their formal oxidation state.

Dynamic loading is a relatively simple way of forming a chelating stationary phase. It requires a small concentration of the chelating compound in the eluent to maintain an equilibrium with a sorbed layer on the stationary phase, and hence the retention of metal ions. The retention of uranium was investigated over a temperature range of 15–30 °C, which reflects typical laboratory ambient conditions. A steady, almost linear, decrease in retention time with increase in temperature was found, declining from 10.1 to 7.8 min. The change in retention time with temperature was considered sufficiently large to warrant thermostating of the column. The column was therefore kept in a water bath set at 30 °C throughout the investigation.

Temperature effects

As dynamic loading is an equilibrium condition involving partitioning between the mobile and stationary phases, it was expected that temperature would affect the equilibrium and hence the retention of metal ions. The retention of uranium was investigated over a temperature range of 15–30 °C, which reflects typical laboratory ambient conditions. A steady, almost linear, decrease in retention time with increase in temperature was found, declining from 10.1 to 7.8 min. The change in retention time with temperature was considered sufficiently large to warrant thermostating of the column. The column was therefore kept in a water bath set at 30 °C throughout the investigation.

Separation characteristics

In an earlier investigation the effect of varying the dipicolinic acid concentration in the eluent from 0.01 to 1 mM was studied. It was found that the effect was relatively small, but a concentration of 0.1 mM produced optimum results for the separation of U and Th, so it was decided to continue to use this concentration level for all the work described here. The key parameter controlling separation in high-performance chelation ion chromatography is the pH. This is because the values of metal complex conditional stability constants change markedly with change in pH. Considering the difficulty in measuring a low pH accurately, pHs below 2 were nominally calculated from the known nitric acid concentration.

Ti(v), Sn(IV), V(IV) and Fe(in) were found not to be retained using eluents over the pH range 0–3. It should be noted that although not investigated, previous studies show that aluminium and lanthanide ions are also not retained over this pH range. A pH higher than 3 was not used because of the appearance of extensive metal hydrolysis, as indicated by severe peak broadening. For the remaining metal ions, Th(IV), U(vi), Zr(IV), Hf(IV), V(IV) and Bi(in), significant retention was obtained, except for Th(IV), which only moved slightly away from the solvent front. Fig. 1 shows the plot of log k’ (capacity factor) against pH for these metals. Apart from Bi(in) they all show a general increase in retention with pH. If metal chelation on the surface of the substrate was the only factor involved then straight line plots would be expected. However, as discussed in previous published work, the presence of the chelating agent in the eluent causes a more complicated relationship, giving
curved plots, with in this case even a reversal of retention for Bi(III). However, lack of data on stability constants of the dipicolinic acid complexes of acid hydrolysing metals makes this behaviour difficult to interpret at present. Nevertheless, this more complex retention behaviour can be exploited where, for example, Bi(III) can be eluted before or after V(IV) depending on pH.

As V(IV) is not retained V(v) is easily separated from V(IV), for example giving a retention time of 5 min at a pH of 1.3, as shown in Fig. 2. This is an interesting finding, as with simple cation exchange in acid media, the reverse is true, V(IV) producing the much greater retention.1 Fig. 3 shows the separation of six metal species at a pH of 0.3 (0.5 M nitric acid). Good efficiencies and peak shapes were obtained, except for pH.

This preliminary study shows that a dipicolinic acid dynamically loaded column can produce good separations of a range of acid hydrolysing metal species in low pH conditions, with a particularly high selectivity for uranium, zirconium and hafnium. The insensitivity to ionic strength, use of strong acid eluents and the lack of retention for Fe(III), Al(III) and the lanthanides, should make this dynamically loaded column particularly suited to the determination of high valence metal ions in complex environmental and biological samples after acid digestion. Further studies are currently being carried out in this area.

Conclusion

References