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Short communication

Comparison of the retention behaviour of uranium and thorium on high-efficiency resin substrates impregnated or dynamically coated with metal chelating compounds

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Abstract

A study of the separation of trace uranium from multi element mixtures using high-performance chelating ion chromatography (HPCIC) is described. Three different chelating columns were compared in the investigations and the results are discussed. Two types of neutral polystyrene substrates were used for forming the chelating surfaces, a hypercrosslinked macronet and a standard low crosslinked polymer. Calmagite, 4-(2-pyridyl) azoresorcinol (PAR) and dipicolinic acid were the chelating compounds selected to impregnate or coat the resins. One unusual finding was the different retention orders for uranium(VI) and thorium(IV) on the three columns. The best separation of uranium(VI) was obtained on the macronet resin dynamically coated with dipicolinic acid. The column gave a uranium peak of good symmetry well separated from thorium(IV), lanthanum(III) and iron(II). The reproducibility of retention and quantitative performance for uranium(VI) was evaluated using arsenazo III post-column reaction detection. © 1998 Elsevier Science B.V. All rights reserved.

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1. Introduction

The determination of uranium and thorium is of particular interest with respect to environmental samples [1] and the nuclear industry [2]. A number of methods have been developed for the determination of uranium and thorium by liquid chromatography. Cassidy and co-workers [1–3] reported uranium separations for the study of uranium dioxide, thorium–uranium dioxide fuels and uranium ore refining processes. α -Hydroxyisobutyric acid (HIBA)

was used as a complexing agent with reversed-phase separations and post-column detection using arsenazo III. Similar methods have been demonstrated by Haddad et al. [4,5] for the determination of thorium and uranium in mineral sands, by Rehkämper [6] for thorium and uranium in geological samples, by Barkley et al. [7] for uranium and thorium in uranium ores and by Kerr et al. [8] for the determination of uranium in natural groundwaters. A variation of this method was also developed by Cassidy et al. [9] using mandelic acid instead of HIBA. Other investigations using ion chromatography include the use of a cation-exchange system

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for the determination of thorium and uranium. This system incorporated the use of a chelating column for preconcentration and matrix elimination from the analytes [10]. Low limits of detection were obtained (typically $1 \mu\text{g l}^{-1}$ for uranium and $3 \mu\text{g l}^{-1}$ for thorium).

Many of the systems mentioned displayed good adsorption, separation and detection qualities for uranium, thorium, or a mixture of both metal ions. However, in complex matrices, i.e., with large amounts of other metal ions present, some of the systems lose their capacity and often become ineffective. An example of this is the HIBA system with a reversed-phase column [1]. In the presence of a high concentration of iron(III) the system loses its ability to separate the uranium from thorium. Some systems require the use of complex matrix elimination steps, but these may be time consuming or can increase the complexity of the adsorption or separation system. A system incorporating a single column, which could separate uranium and thorium in the presence of high ionic strength and relatively high concentrations of other metal ions, would therefore be of great interest. One approach which has the potential for solving these problems, using only a single column, is the use of chelating substrates. These have been used for many years, but almost exclusively in low efficiency preconcentration columns as part of a multi-step isolation and determination process for groups of metal ions. During the last ten years a number of studies have been reported involving analytical separations of metal species on high-performance chelating substrates. A recent review describes the types of high efficiency chelating substrates available, with examples of separations in complex matrices using single columns for the determination of trace metals [11]. To avoid confusion with the term “chelation ion chromatography” which includes methods involving low efficiency substrates in preconcentration columns, the authors use the description “high-performance chelation ion chromatography” (HPCIC). Our approach to the fabrication of high-performance chelating substrates is to impregnate or coat small particle size polystyrene resins with metal complexing compounds, mainly chelating dyestuffs. A comparison of the separation performance of a range of impregnated chelating resins is given by Paull and Jones [12].

Few of the published studies using HPCIC have involved the very heavy elements such as the actinides. It was decided therefore to explore the potential of HPCIC for the investigation of uranium and thorium in complex matrices. The initial stage of the study as presented here was to evaluate HPCIC systems for the separation of uranium(VI) and thorium(IV) using two impregnated and one dynamically coated resin.

A more detailed study was carried out on the dynamically coated resin, where the separation of uranium(VI) from thorium(IV), lanthanum(III) and iron(III) was investigated, together with a quantitative assessment for trace uranium determination using arsenazo III post-column detection.

2. Experimental

2.1. Instrumentation and HPCIC conditions

The basic instrumentation used for HPCIC has been described in a previous study by Sutton et al. [13] and is based on a standard HPLC set-up incorporating post-column reaction detection. For the Calmagite- and dipicolinic acid-coated columns, a Dionex GP40 inert gradient pump (Dionex, Sunnyvale, CA, USA) was used to deliver the mobile phase at 1 ml min^{-1} . Refer to the text and figure legends for the eluent compositions used. A Rheodyne 9010 six-port injector (Rheodyne, Cotati, CA, USA) was used to inject the samples via a $100\text{-}\mu\text{l}$ sample loop. The post-column reagent was either, $2 \cdot 10^{-4} \text{ M}$ arsenazo III (Fluka, Dorset, UK) in 3.6 M HCl , with 1% Triton X-100 (BDH) or, $2 \cdot 10^{-4} \text{ M}$ arsenazo III in 1% Triton X-100, delivered by a Constametric (III) pump (LDC, Milton Roy) at 1 ml min^{-1} . Detection was carried out using a Spectral Array Detector (Dionex, UK), set at 654 nm .

The 4-(2-pyridyl) azoresorcinol (PAR) column studies were performed in another laboratory where the eluent pump was a P-500 syringe pump (Pharmacia, Barcelona, Spain) and the post-column reagent was delivered with a Minipuls-2 peristaltic pump (Gilson, Seville, Spain). In addition, a glass column ($100 \text{ mm} \times 2 \text{ mm I.D.}$) packed with lead filings was incorporated into the system between the analytical column and the zero dead volume T-piece

to facilitate the on-line reduction of U(VI) to U(IV). The detector was an LKB 2151 variable-wavelength monitor set at 665 nm (Bromma, Sweden).

2.2. Preparation of small particle size MN200 hypercrosslinked resin

The MN200 (Purolite, Hengoed, UK) was crushed and fractionated using fine mesh sieves and centrifugation. The mean particle size was measured using a Malvern Mastersizer 2.1 (Malvern Instruments, Malvern, UK).

2.3. Column preparation

All resins were packed into polyether ether ketone (PEEK) columns 100 mm×4.6 mm I.D. The Calmagite-impregnated column was prepared by Paull and Jones [12] using 8.8 μm high-performance reversed-phase polystyrene resin (Dionex). The PAR-impregnated column was prepared as described in the paper by Sutton et al. [13], using a column packed with 20 μm MN200. The column used for dynamically coating with dipicolinic acid was packed with MN200 crushed to a mean particle size of 10 μm .

2.4. Reagents

All reagents unless stated were of “AnalaR” grade (BDH, Poole, UK) and were diluted to various concentrations by simple dilution with distilled, deionised water from a Milli-Q (Millipore, USA) water purification system. Uranium(VI) and thorium(IV) standards were prepared by serial dilution of 1000 mg l⁻¹ commercially available spectroscopic standards (Johnson Matthey, UK).

3. Results and discussion

3.1. Calmagite column

The Calmagite column is typical of the range of chelating dyestuff-impregnated columns produced by Jones and co-workers and a comparative study of the most successful types has been published. [12]. The polystyrene resin substrate used is similar to that sold

commercially for reverse phase separations. The crosslinking is less than 10% and the pore size approximately 100 Å. The specific polymer in this case was supplied by the Dionex Corporation. The Calmagite column was chosen for study as the dye contains an α,α' -dihydroxyazo grouping which should give chelation with uranium and thorium at low pH values. High concentrations of potassium nitrate were used in the eluents to suppress simple ion-exchange interactions to make sure that chelation-exchange was the only major sorption mechanism operating [11].

Initial studies with 0.5 M potassium nitrate eluents containing nitric acid showed that retention of U(VI) started to occur only when the acid concentration was less than one molar. Unfortunately, thorium was very strongly held at these lower acid concentrations. The addition of oxalic acid shortened the retention time of thorium sufficiently, but also made the uranium elute on the solvent front. A step gradient was therefore required with oxalic acid present in the final eluent. An example chromatogram is shown in Fig. 1. The lead reduction column was not used in the post-column reaction detection system (see Section 3.2) as it was not compatible with oxalic acid. The arsenazo III reaction was therefore carried out at pH 2 where U(VI) reacts, though less sensitively.

Clearly, the Calmagite column showed a very large selectivity difference between U and Th. This could be overcome by using a gradient, but isocratic separations are generally more convenient. Furthermore, the U peak broadened considerably when only a small distance from the solvent front. It was therefore decided to evaluate other chelating substrates to see if isocratic separations could be obtained.

3.2. PAR column

This column was one of a number of chelating columns prepared using neutral, hypercrosslinked polystyrene resins called macronets. The so-called macronets are highly crosslinked polystyrene resins, usually greater than 60%, made in such a way as to maintain an open porous structure. Earlier studies using the resin suggested that greater chelating dye loadings were achievable during impregnation compared to a standard lower crosslinked resins such as

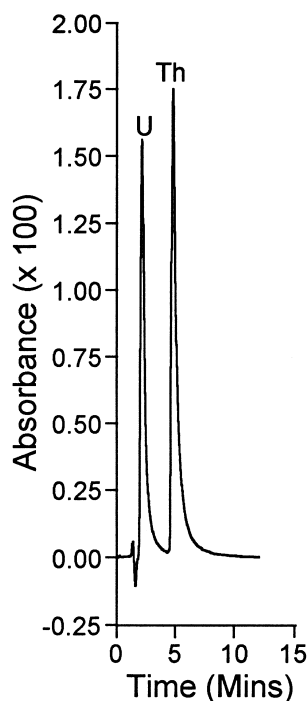


Fig. 1. A 100- μ l injection of 2 mg l^{-1} U(VI) and 2 mg l^{-1} Th(IV) using the 8.8 μ m polystyrene Calmagite impregnated column. The initial eluent was 0.5 M KNO_3 and 0.1 M nitric acid followed after 3 min with the addition of 0.01 M oxalic acid. Detection was with arsenazo III at 654 nm.

the Calmagite impregnated column discussed above. The macronet supplied by Purolite (MN200) was of large particle size and needed to be crushed to much smaller particles to achieve reasonable separation efficiencies.

The fabrication and study of the PAR-loaded macronet column has been described in previous work [13], where a separation of four alkaline earth metal ions was achieved. The strong chelating nature of PAR in acid solution indicated that it would have potential for separating metal ions such as uranium(VI) and thorium(IV) which are strongly hydrolysed above pH 2. After a series of preliminary tests, the PAR column appeared stable in acidic media and was considered suitable for the investigation of uranium and thorium separations.

For detection, the arsenazo III post-column reaction system as reported by Pavon et al. [14] was used, prepared in 3.6 M HCl, since this concentration produced the most sensitive and selective reaction

for uranium and thorium. However, U(VI) would not react at such a low pH and a 100 mm Pb reduction column was prepared to reduce U(VI) to U(IV) after elution from the PAR separating column and before mixing with the arsenazo III reagent.

A preliminary investigation with nitric acid eluents soon revealed that the PAR column had a much stronger affinity for uranium(VI) than the Calmagite column with retention times of about 10 min in 1 M nitric acid. Potassium nitrate was dispensed with in further studies as these high concentrations of acids were sufficient to suppress simple ion-exchange effects. What was particularly interesting was that the retention order was reversed compared to Calmagite with thorium eluting on or close to the solvent front.

Fig. 2 shows a separation of Th and U using a 1.5 M nitric acid eluent. The pulsing baseline was due to the peristaltic pump used to deliver the arsenazo III reagent. The peak shape for the uranium was quite reasonable when considering that the average particle size was 20 μ m. Unfortunately, small amounts of the

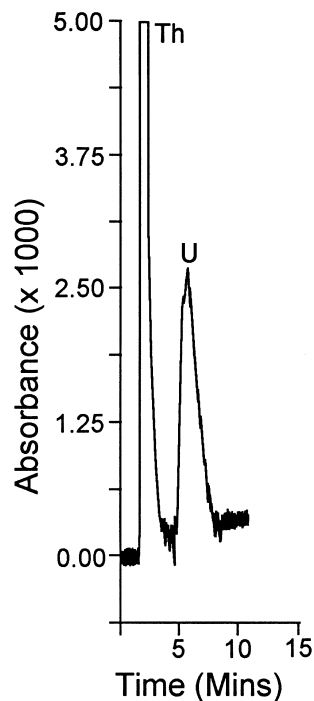


Fig. 2. A 100- μ l injection of 200 μ g l^{-1} U(VI) and 200 μ g l^{-1} Th(IV) using the 20 μ m MN200 PAR column. The eluent was 1.5 M HNO_3 and detection was with arsenazo III at 665 nm after reduction on a lead column.

PAR coating bled from the column at the high acidities used causing a steady shortening of retention times. Therefore in spite of the promising nature of the selectivity of separation, the PAR studies were temporarily abandoned while other chelating systems were investigated.

3.3. Dipicolinic acid column

During our continuing studies of macronet resins it has become evident that they show unusual and sometimes unexpected properties compared to the “normal” low crosslinked polystyrene based polymers. One such discovery was that the bare resin, i.e., not impregnated or coated with chelating groups, showed strong adsorption for some metal ions in high ionic strength media. This has also been reported by Davankov et al. [15], one of the pioneers in the development of hypercrosslinked resins. Bismuth(III) for example is strongly retained by bare MN200 and this property has recently been exploited for the determination of bismuth in lead [16]. The bare MN200 was therefore investigated for the adsorption of uranium(VI) and thorium(IV). However, although retention of uranium did occur, it was eventually established that the observed retention was actually caused by adsorbed dipicolinic acid used previously in column clean-up procedures. However, the dipicolinic acid coating was not that stable and very slowly diminished with a parallel decrease in uranium retention times. One way to prevent this and stabilize a coating is to add a small amount of the chelating compound to the eluent so that an equilibrium is set up between the amount adsorbed on the substrate and the concentration in the mobile phase. This has become known as dynamic coating and a number of studies have shown that good stable chromatographic conditions can be achieved in this way. For example Paull et al. [17] used a dynamic coating of methyl thymol blue (MTB) on porous glassy carbon to separate alkaline earth metal ions and determine them in brines. The concentration of dipicolinic acid in the eluent greatly affected the retention of uranium while thorium always remained close to the solvent front, though with significant tailing. It should be mentioned that the elution order is the same as that for the PAR column and opposite to the Calmagite column. Both

PAR and dipicolinic acid have a pyridyl nitrogen which takes part in the metal complex formation and might explain why they show similar affinities for uranium(VI) and thorium(IV). After a number of studies a concentration of $4 \cdot 10^{-4}$ M dipicolinic acid in the eluent was shown to give optimum separation with a clear separation of uranium from thorium in under 15 min. Since nitrate in the eluent had a small but significant effect on the retention of uranium, probably due to the formation of a uranium nitrate complex, perchlorate was substituted in further studies.

3.4. Separation performance on the dipicolinic acid column in the presence of lanthanum and iron

Further studies were carried out evaluating the retention of lanthanum(III) and iron(III) on the dynamically coated resin. These two metals are associated with uranium and thorium in mineral deposits and can cause problems in isolation and determination procedures. Both lanthanum(III) and iron(III) were found to elute early close to the solvent front, similar to thorium. Thus, the dipicolinic acid coated column appears to be very selective for uranium and shows potential for its determination in the presence of these metals. However, when iron(III) was present in relatively large amounts, as it is likely to be in actual samples, severe tailing was observed which interfered with the uranium peak. Because of this it was decided to investigate mixed metal mixtures with the addition of ascorbic acid to reduce iron(III) to iron(II). When this was done no peak was observed for the iron as iron(II) does not react with arsenazo III at such low pH values.

To test the chromatographic and quantitative performance of the dynamic coating a series of uranium standard additions were performed on a mixture of 500 mg l^{-1} Fe(III), 10 mg l^{-1} La(III) and 2 mg l^{-1} Th(IV). The combined chromatograms are shown in Fig. 3. The constant retention times found clearly indicated stable chromatography. Good quantitative performance was also displayed. The calibration plot was very linear with a correlation coefficient of 0.99998 and the reproducibility was 1.9% relative standard deviation for seven repeat injections of a 2 ppm uranium sample.

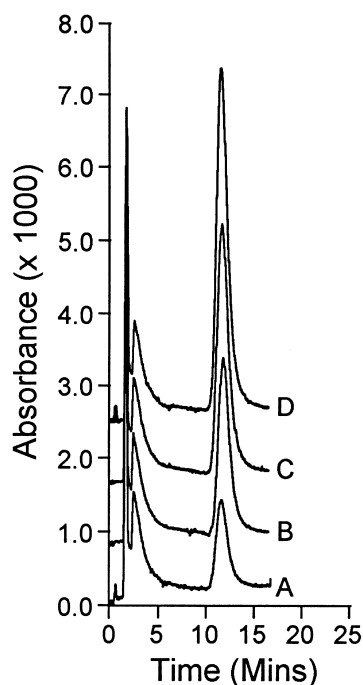


Fig. 3. Overlaid chromatograms of standard additions of U(VI) to a mixture of 500 mg l^{-1} Fe(III), 10 mg l^{-1} La(III) and 2 mg l^{-1} Th(IV) containing ascorbic acid using the dynamically coated dipicolinic acid column. A, B, C and D are 2, 4, 6 and 8 mg l^{-1} uranium, respectively. The eluent was 1.0 M perchloric acid and 1.0 M sodium perchlorate containing $4 \cdot 10^{-4} \text{ M}$ dipicolinic acid. Detection was with arsenazo(III) at 654 nm .

4. Conclusions

The Calmagite column gave the expected retention order for uranium(VI) and thorium(IV), but was particularly selective for thorium, requiring a gradient to determine both peaks in a reasonable time. The PAR and dipicolinic acid columns produced a more reasonable difference in selectivity, but unexpectedly gave a reverse retention order. The column dynamically coated with dipicolinic acid gave the best results for the separation of uranium

(VI) from thorium(IV), lanthanum and moderately high levels of iron. The thorium(IV) peak was too close to the solvent front for reliable quantitative estimations to be carried out. Uranium(VI) on the other hand gave stable retention times and good quantitative performance with arsenazo III post-column detection. Further studies are underway to evaluate the dipicolinic column for the determination of uranium in mineral samples.

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