Separation of Actinides Using Capillary Extraction Chromatography–Inductively Coupled Plasma Mass Spectrometry*

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Abstract

Trace levels of actinides have been separated on capillary extraction chromatography columns. Detection of the actinides was achieved using an inductively coupled plasma mass spectrometer, which was coupled with the extraction chromatography system. In this study, we compare 30-cm long, 4.6 mm i.d. columns to capillary columns (750 µm i.d.) with lengths from 30 cm up to 150 cm. The columns that were tested were packed with TRU resin. We were able to separate a mixture of five actinides (^{232}Th, ^{238}U, ^{237}Np, ^{239}Pu, and ^{241}Am). This work has application to rapid bioassay as well as automated separations of actinide materials.

Introduction

The concentration of actinides in human urine can be used to determine if an individual has had an intake of actinide materials. Traditionally, this type of analysis has been used to routinely monitor the occupational exposure of nuclear energy and nuclear weapons workers. The actinide elements are considered very toxic due to their long half-lives, alpha radioactivity, and their chemical toxicity. There is currently a concern that a radiological dispersal device could be used to expose a population to radioactive materials. These types of elements can enter the body through inhalation, ingestion, or through wounds where even a small exposure can cause health hazards. Because of these potential exposure modes and the need to test a large population, a rapid screening method is needed to analyze for actinides in urine.

A variety of analytical techniques have been used to detect very low concentrations of actinides. These methods include neutron activation analysis, alpha spectrometry, thermal ionization mass spectrometry, and fission track analysis. These analysis methods required significant amounts of sample, and the sample preparation and sample analysis is time consuming. An alternative method that has recently received study is inductively coupled plasma mass spectrometry (ICP-MS), which is useful for actinide analysis (1). Analysis time is short and detection limits are low (parts-per-quadrillion) (2,3). These low detection limits are better than many other analysis techniques (4). However, low resolution ICP-MS is susceptible to isobaric interferences and polyatomic interferences (5,6). Analysis of very complex solutions is difficult and these analyses are much less sensitive than on neat solutions. The lower sensitivity is due to the large numbers of matrix ions that are present in complex solutions. Low detection limits can still be achieved, but it requires that the undesired ions be separated from the analytes prior to introduction into the ICP-MS. Separating analytes that can interfere isobarically will also enable improved detection limits, especially with lower resolution ICP-MS instruments.

The separation of actinides prior to analysis is important for both alpha spectroscopy and for ICP-MS analysis (7). Chemical separation methods are time-consuming processes, and there is a great value in automating these processes to enable a more rapid analysis process. One approach that has been used is to load a commercial actinide specific resin using flow injection analysis and then strip the actinides after the interfering matrix ions have been removed (8). Several resins have been described for actinide separations by immobilizing liquid extractants on polymer beads. Some of the resins that have been developed are TRU (9), U/TEVA (10), and TEVA (11). Our laboratory has recently demonstrated a separation of five actinides on columns prepared with TRU or U/TEVA columns (12). We have also examined how various packing parameters affect the quality of separations for columns packed with TRU resin (13). Although we previously examined the effect of length on 4.6 mm i.d. columns, we did not examine the effect that smaller diameter columns have on the separation performance.

In this study, we have packed columns with TRU resin and used them to separate actinides. We have packed columns 4.6-mm i.d. and 30-cm long. We have also packed columns 750-µm i.d. with lengths 30 cm, 100 cm, and 150 cm.

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Experimental

Instrumentation

IC was performed using a high-performance ion chromatograph (DX-600, Dionex, Sunnyvale, CA). The IC was equipped with an autosampler (AS50, Dionex) capable of injections up to 1 mL. Elemental detection and identification of the IC eluent was accomplished by a quadrupole ICP-MS (Elan 6100, PerkinElmer, San Jose, CA). Typical parameters for the ICP-MS were: 0.75 L/min nebulizer gas flow, 10.25 V lens voltage, 1225 W ICPRF power, –2200 V analog stage voltage. The ICP was equipped with an Apex-Q inlet system (Elemental Scientific, Omaha, NE). This inlet system uses a MicroFlow PFA nebulizer followed by a condensation chamber. This approach leads to a lower background and improved sensitivity. The process of sample injection, separation, and detection was automated through the Chromeleon management system (Dionex), and the ICP-MS software was triggered to collect data through a contact closure. Data was collected by peak hopping between the major actinide masses (^{232}Th, ^{238}U, ^{237}Np, ^{239}Pu, and ^{241}Am).

Reagents and materials

Trace metal-grade nitric acid was obtained from Fisher Scientific (Pittsburgh, PA). Oxalic acid eluent was purchased from Dionex and diluted to the recommended concentration (80 mM oxalic acid, 100 mM tetramethyl ammonium hydroxide, and 50 mM potassium hydroxide). Deionized water (18 MΩ, Nanopure Water System, Barnstead, Dubuque, IA) was used to dilute acids and standards to the desired concentrations. IC columns were prepared using a resin containing octylphenyl-*N,N*-diisobutyl carbamoylphosphine oxide adsorbed onto the packing beads, which are made of polymethylmethacrylate. This resin is commonly called TRU resin and was obtained from Eichrom Technologies (Darien, IL). These resins were supplied with the smallest available size: 20–50 µm. Standard column preparation involved packing the resin PEEK lined column hardware (Alltech Associates, Deeerfield, IL) using an Alltech model 1666 Slurry Packer.

Standard columns were prepared in 30 cm lengths, and all columns had an inside diameter of 4.6 mm. Capillary columns were prepared in capillary PEEK tubing obtained from Upchurch Scientific, Inc. (Oak Harbor, WA). PEEK tubing used was 0.030 in i.d. (762 µm). Upchurch hardware was used to connect the capillary tubing to the analytical system. A Frit-in-a-ferrule (2 µm) was used to contain the resin within the capillary.

Standard solutions of ^{237}Np, ^{239}Pu, and ^{241}Am were obtained from Isotope Products (Valencia, CA). These standards are normally sold with a specific activity (i.e., 2 µCi/mL, equal to 74,000 Bq/mL), so these values were converted to parts-per-million (ppm) values so that all standards would be prepared with similar values. A standard 1000 ppm ICP-MS solution of Th was obtained from Alfa Aesar (Ward Hill, MA). A standard 1000 ppm ICP-MS solution of U was obtained from SPEC Certiprep (Methchen, NJ). The thorium solution was confirmed to contain 100% of ^{232}Th, the uranium solution was confirmed to contain approximately 0.7% ^{235}U and 99.3% ^{238}U (natural uranium concentrations). All actinides were diluted to a stock solution of 50 parts-per-trillion (ppt) in water with 5% nitric acid. Further standards were prepared from dilutions of the stock solution. Some injections included an overspike of thorium to improve the detection of that analyte.

Column preparation

Standard columns were prepared using an Alltech Model 1666 slurry packer in order to maintain the reproducibility of the packing from column to column. The slurry packer contains a pneumatic amplification pump which enables a low pressure gas supply to be amplified into the liquid of the slurry. The amplification is approximately 1:100. To pack the column, the resin was first suspended in ~ 25 mL of deionized water. The slurry was mixed overnight prior to packing. The column and exit frit were then attached to the reservoir, into which the packing slurry was added. The reservoir was topped off with deionized water, and the fluid lines from the slurry packer were attached to the reservoir. After the lines were primed, the air pressure was adjusted to the desired level and the solvent flow was turned on. The slurry packer was allowed to pack each column for approximately five minutes. After the pressure was bled off, frits were installed and the column was rinsed with a flow of 3 M nitric acid at a flow rate of 3 mL/min for 20 min.

Capillary columns could not be packed using the slurry packer. Capillary column packing was performed by dispersing the resin in water and placing in a reservoir connected to the capillary. The resin was first allowed to fill the capillary by gravity for 2 h. After this, ultrasonic agitation for 6 h was used to fully pack the column using a Fisher Scientific Ultrasonic bath operating at a frequency of 43 kHz and a power of 225 W. During this process, the column was kept in a vertical position. Packing was performed at room temperature. After packing, the second frit was installed and the column was rinsed with 3 M nitric acid for 20 min.

Results and Discussion

Our previous studies have demonstrated the use of packed columns for the separation of actinides in bioassay matrices prior to analysis using ICP-MS. We have packed dozens of columns and optimized these columns. The optimized gradient is given in Table I. A typical separation using a 30-cm long 4.6-mm i.d. column is shown in Figure 1. This shows good separation between the five actinides in under 15 min. While our previous study examined the effect of column length, this study examines the effect of column diameter.

In order to study the effect of column diameter on the separation of actinides, we packed polymer capillary tubing with an extractive resin. Our first column tested was a 30-cm long column. The separation gradient is the same as in Table I, but with a flow rate of 0.75 mL/min. Table II shows the flow rate, backpressure, bed volume for each capillary column, and the linear velocity for each given flow rate. This produced a poor separation, particularly between Pu and U, which are two analytes that are important to have a good separation. The

reason for the poor separation in the 30-cm long column is likely due to the high linear velocity, which also resulted in limited contact time between the analytes and the resin.

In order to improve the separation, we then packed a capillary column 100-cm long. Because of the increase length, the backpressure went up significantly, so a lower flow rate through the column was possible, which also results in a lower linear velocity of solvent through the column. This column was used to separate the five actinides and is shown in Figure 3. This data shows a very good separation between the five actinides (with americium and plutonium slightly overlapping) in under 15 min. The quality of this separation is superior to the standard size 30-cm column, even though the flow-rate is 1/3 that of the larger column. We also examined the column-to-column reproducibility by having a second analyst pack a 100-cm long column and use it to separate the actinides. This column produced a separation of similar quality to that shown in Figure 3 indicating that the column-to-column reproducibility is very good.

Because of the good results obtained with a 100-cm long column, we also packed a 150-cm long column and used it to separate the mixture of five actinides. The flow-rate for these separations had to be even lower to keep the backpressure to an acceptable level. This separation is shown in Figure 4. While the first three actinides (Np, Am, and Pu) are well-separated, the Th and U show significant dispersion. This is not unexpected, considering the difficulties encountered in packing the longer column.

The obvious next experiments would involve packing and performing separations using capillary tubing with smaller

Table I. Gradient Used in this Study

Time (min)	Flow (mL/min)	Eluent
Gradient 1		
–2	1.5	3 M HNO
0	1.5	2 M HCl, 40%; $H_2C_2O_4$ 60
6	1.5	2 M HCl, 0.5%; H_2O 59.5%; $H_2C_2O_4$ 40%
12	1.5	2 M HCl, 0.5%; H_2O 59.5%; $H_2C_2O_4$ 40%

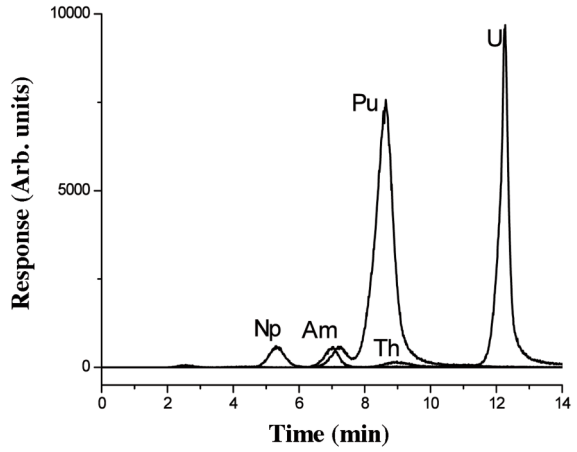

Figure 1. Separation of actinide analytes on 30-cm long column, 4.6-mm i.d. packed with TRU resin. The sample contained 50 ppt of each actinide, 400 µL injected. Separation gradient conditions are listed in Table I.

Table II. Flow-Rates and Backpressure for Capillary Columns

Length	Flow-rate	Linear velocity	Backpressure	Bed volume
30 cm	0.75 mL/min	42 cm/min	800 psi	0.5 mL
100 cm	0.5 mL/min	28 cm/min	1500 psi	1.7 mL
150 cm	0.25 mL/min	14 cm/min	1600 psi	2.5 mL

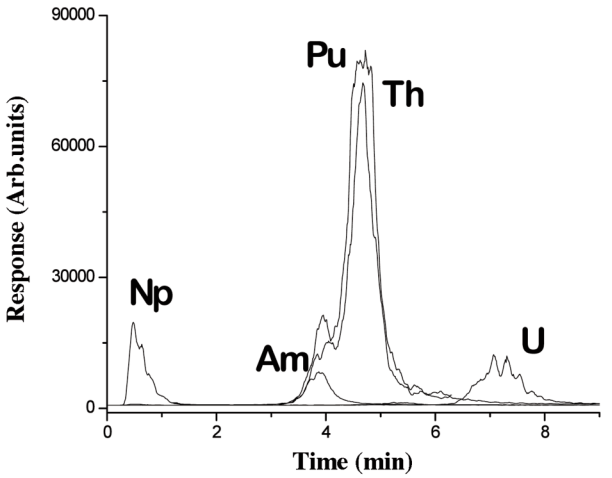

Figure 2. Separation of actinide analytes on 30-cm long column, 750 µm i.d. packed with TRU resin. The sample contained 50 ppt of each actinide, 200 µL injected. Separation gradient conditions are listed in Table I, flow-rate is listed in Table II.

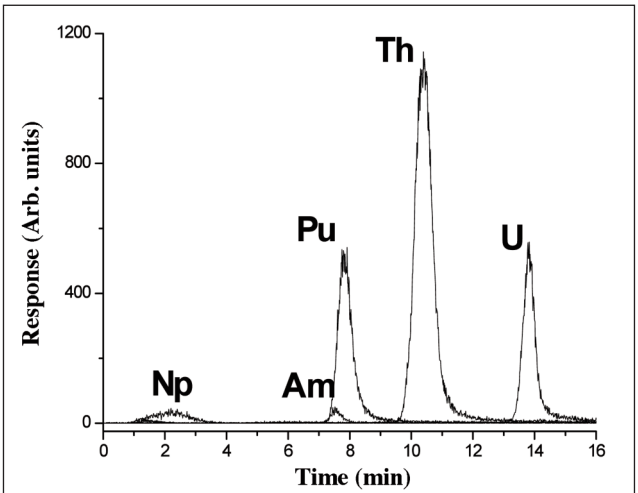

Figure 3. Separation of actinide analytes on 100-cm long column, 750 µm i.d. packed with TRU resin. The sample contained 50 ppt of each actinide except thorium, which contained 300 ppt; 400 µL injected. Separation gradient conditions are listed in Table I, flow-rate is listed in Table II.

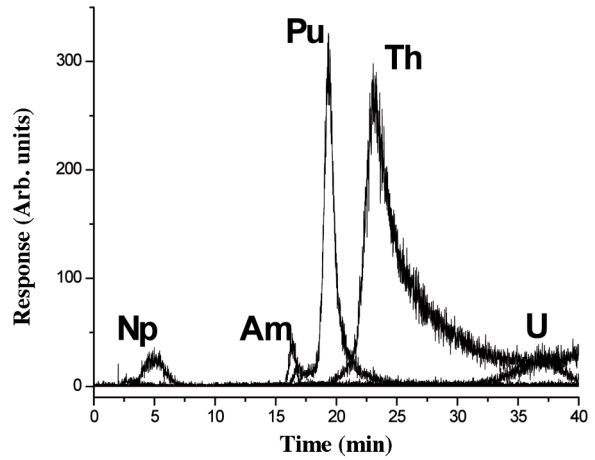

Figure 4. Separation of actinide analytes on 150-cm long column, 750-µm i.d. packed with TRU resin. The sample contained 50 ppt of each actinide except thorium, which contained 300 ppt; 200 µL injected. Separation gradient conditions are listed in Table I, flow-rate is listed in Table II.

diameters. We attempted to pack 500-µm and 250-µm i.d. capillaries. These columns produced very high backpressures, but we were unable to obtain a suitable separation of the actinides using these columns. If these columns become desirable, an alternative method for packing the columns will need to be developed.

Concluding Remarks

In this study, we have demonstrated the on-line separation of actinides on columns prepared in capillary columns using TRU resin. The columns were coupled to an ICP-MS spectrometer for detection. The shorter column did not produce a good separation, likely due to the high linear velocity used. The longest column resulted in extended times for analysis, and significant band broadening was observed for the later eluting analytes. The best results were seen with the 100-cm long column, which produced a better separation in the same amount of time compared to the standard columns (4.6 mm i.d.). This separation approach produces a method that uses less solvent and less analyte solution and therefore capitalizes on the advantages of microfluidics to produce high quality data very rapidly. This approach is very suitable to coupling with the Apex desolvation inlet to produce detection limits in the low ppt for a quadrupole ICP-MS.

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