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Author(s):	Dominic S. Peterson Velma M. Montoya
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Separation of actinides using capillary extraction chromatography-inductively coupled plasma mass spectrometry [1]

Dominic S. Peterson*, Velma M. Montoya

Chemistry Division, Los Alamos National Laboratory

Corresponding Author:

Dominic S. Peterson

Mailstop K484

Los Alamos National Laboratory

Los Alamos, NM 87545

DominicP@lanl.gov

(505)665-3320

Fax: (505)665-5982

Abstract

Trace levels of actinides have been separated on extraction chromatography columns. Detection of the actinides was achieved using an inductively coupled plasma mass spectrometer (ICP-MS), which was coupled with the extraction

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chromatography system. In this study we compare 30 cm long, 4.6 mm ID columns to capillary columns (750 μm ID) 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, ^{241}Am). This work has application to rapid bioassay as well as for 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 (RDD) 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, the

sample preparation and sample analysis is time consuming, and instrumentation can be expensive. An alternative methods that has recently received study is inductively coupled plasma mass spectrometry (ICP-MS), and is useful for actinide analysis.[1] Analysis time is short and detection limits are low (PPQ). [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 5 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 ID 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 ID and 30 cm long. We have also packed columns 750 μm ID with lengths 30 cm, 100 cm, and 150 cm.

Experimental

Instrumentation

Ion chromatography 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 quadrapole ICP-MS (Elan 6100, Perkin Elmer, San Jose, CA). Typical parameters for the ICP-MS were: 0.75 L/min nebulizer gas flow, 10.25 V Lens Voltage, 1225 W ICP-RF 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, ^{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

Ion Chromatography 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. These extractants were adsorbed onto the packing beads, which are made of poly(methyl methacrylate). 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 Upchrch Scientific, Inc. (Oak Harbor, WA). PEEK tubing used was 0.030"ID (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^{-1}, equal to 74,000 Bq mL^{-1}), so these values were converted to 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 ppt in water with 5% nitric acid. Further standards were prepared from dilutions of the stock solution.

Column Preparation

Standard columns were prepared using an Alltech (Columbia, MD) 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 a column the resin was first suspended in approximately 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 3M nitric acid at a flow rate of 3 ml/min for 20 minutes.

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 hours. After this, ultrasonic agitation for 6 hours was used to fully pack the column. After packing the second frit was installed and the column was rinsed with 3M nitric acid for 20 minutes.

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 have optimized these columns. The optimized gradient is given in Table 1. A typical separation using a 30 cm long 4.6 mm ID column is shown in Figure 1. This shows good separation between the five actinides in under 15 minutes. 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 1, but with a flow rate of 0.75 ml/min. Table 2 shows the flow rate, backpressure, and bed volume for each capillary column. 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 is the limited amount of resin available to separate the analytes on . The bed volumne of a 30 cm long 4.6 mm ID column is approximately 20 mL. The bed volume for a 30 cm long 0.75 mm ID column is 0.5 mL.

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. 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 in under 15 minutes. 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 5 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 as the time required to fully elute the U is nearly 40 minutes and significant band broadening can be expected at these time scales, particularly with the flow rate at 0.25 mL/min.

The obvious next experiments would involve packing and performing separations using capillary tubing with smaller diameters. We attempted to pack 500 μm and 250 μm ID 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 limited bed volume available. 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 ID). 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 parts per trillion for a quadrapole ICP-MS.

Acknowledgements

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Table 1: Gradient used in this study

Gradient 1		
Time (min)	Flow (mL min^{-1})	Eluent
-2	1.5	3M HNO_3
0	1.5	2M HCl, 40%; $H_2C_2O_4$ 60%
6	1.5	2M HCl, 0.5%; H_2O 59.5%; $H_2C_2O_4$ 40%
12	1.5	2M HCl, 0.5%; H_2O 59.5%; $H_2C_2O_4$ 40%

Table 2: Flow rates and backpressure for capillary columns

Length	Flow Rate	Backpressure	Bed volume
30 cm	0.75 ml/min	800 psi	0.5 mL
100 cm	0.5 ml/min	1500 psi	1.7 mL
150 cm	0.25 ml/min	1600 psi	2.5 mL

Figure Captions

Figure 1: Separation of actinide analytes on 30 cm long column, 4.6 mm ID packed with TRU resin. Sample contained 50 ppt of each actinide, 400 μL injected. Separation gradient conditions listed in Table 1.

Figure 2: Separation of actinide analytes on 30 cm long column, 750 μm ID packed with TRU resin. Sample contained 50 ppt of each actinide, 200 μL injected. Separation gradient conditions listed in Table 1, flow rate listed in Table 2.

Figure 3: Separation of actinide analytes on 100 cm long column, 750 μm ID packed with TRU resin. Sample contained 50 ppt of each actinide except Thorium, which contained 300 ppt; 400 μL injected. Separation gradient conditions listed in Table 1, flow rate listed in Table 2.

Figure 3: Separation of actinide analytes on 150 cm long column, 750 μm ID packed with TRU resin. Sample contained 50 ppt of each actinide except Thorium, which contained 300 ppt; 200 μL injected. Separation gradient conditions listed in Table 1, flow rate listed in Table 2.

Figure 1
Standard column separation

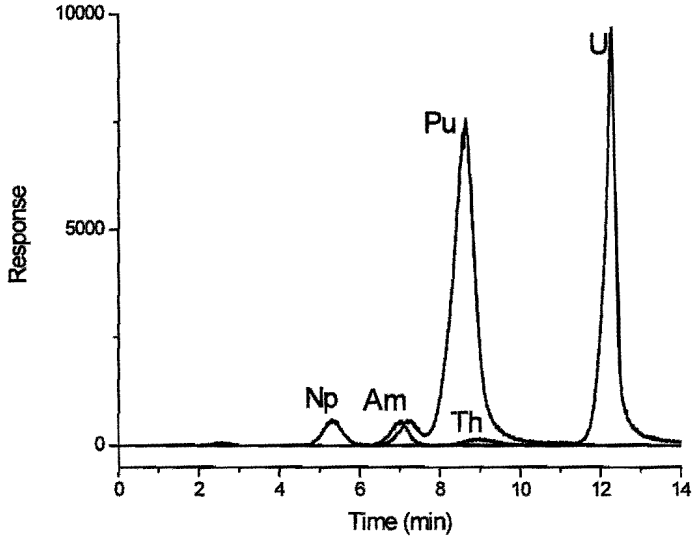

Figure 2
30 cm capillary column

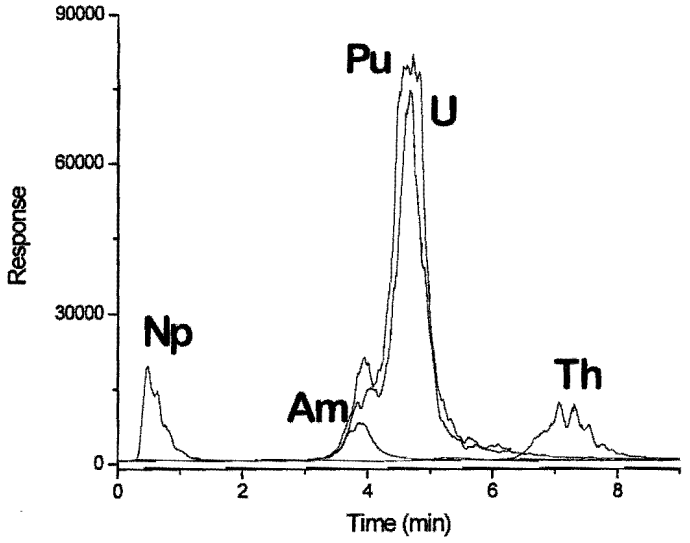

Figure 3
1 m column

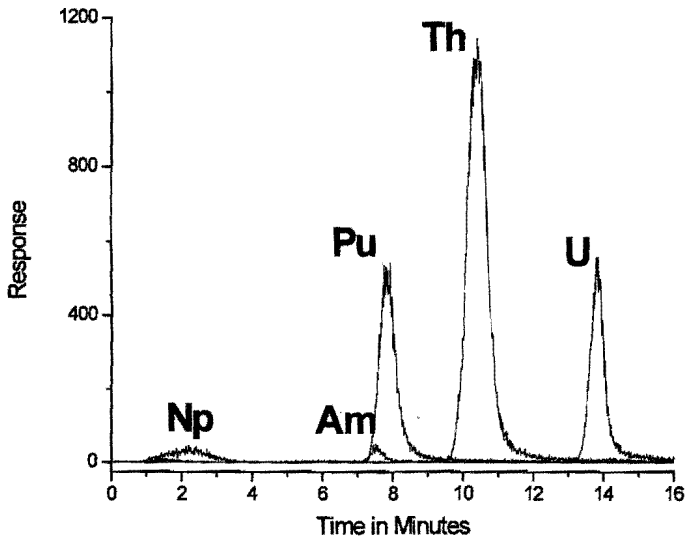

Figure 4
1.5 m column