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DETERMINATION OF ACTINIDES IN URINE BY LIQUID ION EXCHANGE

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Determination of Actinides In Urine By Liquid Ion Exchange

Introduction

The need for analytical methods to determine the actinides separately, and as mixtures, will increase as production of the transplutonium elements increases.

Liquid ion exchange is a relatively new technique for the chemical analysis of urine samples. In this method an aqueous sample is extracted with an exchanger dissolved in an inert solvent. Nuclides as anions and cations are substituted at exchange sites in the liquids similar to absorption by solid ion exchangers[1]. An advantage of liquid ion exchange is the rapidity of both absorption and desorption of ions.

Anion and cation exchange reactions used to separate the alpha-emitting actinides Th, Np, U, Pu, Am, and Cm, are described in this paper. Methods of analyzing urine for specific actinides are presented.

Discussion

Liquid Exchangers Tested

Three exchangers were used in experiments. One was di-2-ethylhexyl phosphoric acid (HDEHP), an acidic cation exchanger. The others were tri-isooctylamine (TIOA) and "Alamine-336," both tertiary amines which function as anion exchangers. Because preliminary experiments showed that the amine extractions gave similar results, only TIOA will be discussed here.

Screening Experiments with Aqueous Solutions

The actinides were separated initially with solutions containing various concentrations of HNO_3 and HCl. Samples were spiked and small aliquots were counted for alpha or gamma activity, before and after extraction. Similar tests were made to strip the actinides from the organic phases.

Conditions were sought for quantitative separation of a specific actinide with good decontamination for the other nuclides. Some of the variables studied were:

- Concentrations of exchangers in inert solvents.
- Volume ratios of the sample, organic, and stripping solutions.
- Acidity of the sample solutions.
- Contact times of the solutions.
- Valences of the actinides.

Analysis of Urine

When analytical methods using aqueous solutions showed promise, additional tests with urine samples were made. Samples were prepared for analysis by wet ashing (oxidizing) them to a white residue. Initially, composite urine samples up to 250 ml were analyzed. Separation procedures were finally tested with individual samples. The valences of the actinides in the wet oxidized urine samples were not adjusted except for the Np and Pu procedures.

Exchange with TIOA

Slide 1 shows extractions of aqueous sample solutions with 10% TIOA in xylene. All extraction times were one minute and equal volumes of sample and organic solutions were used. Only uranium was exchanged almost completely from 3N HCl solution; both Np and Pu were extracted at higher HCl concentrations. Th, Am, and Cm did not form exchangeable anionic complexes with HCl. Th, Np, U, and Pu were partially exchanged from 4N HNO_3.

▶ ENRICHED URANIUM

Other tests were made to determine the best solution for extracting U^{235} absorbed in 75 ml of 10% TIOA-xylene. Two successive one-minute extractions with 20 ml of distilled water removed 88% and 12% of the U^{235}.

Experiments with urine samples resulted in the following procedure (Slide 2). Urine was wet ashed to a white residue and dissolved in 50 ml of 3.5N HCl. The sample was extracted in a separatory funnel for 2 minutes with 50 ml of 10% TIOA-xylene. It was then transferred to a second funnel and extracted with 25 ml of 10% TIOA-xylene. Organic phases were combined and washed with 15 ml of 3.5N HCl, which was discarded. The wash solution removed traces of urine salts and other actinides. U^{235} was then stripped from the TIOA with two 25-ml volumes of distilled water. The water was evaporated, and the residue was plancheted and counted.

Final planchets contained less than 5 mg of solids, and recoveries of U^{235} spikes at levels down to 10 d/m per sample were greater than 95%. Decontamination factors for other actinides were greater than 1000. Total preparation time after dissolution of the oxidized urine salts was less than one hour per sample.

▶ NEPTUNIUM AND PLUTONIUM

Slide 1 also shows some extraction of Np and Pu from HNO_3 solution to TIOA-xylene. Tests indicated that valence adjustments were necessary for complete exchange of the two actinides. Pu (III) will not exchange, but Np (IV), Pu (IV), and Pu (VI) will exchange to $TIOA^2$. Slide 3 shows three ways to extract Np or Pu. Ammonium iodide reduced plutonium to Pu (III) which was not extracted from concentrated HCl, but more than 99% of Np (IV) was extracted. This procedure could not be used for urine, however, since the salts will not dissolve in concentrated HCl. Ferrous ammonium sulfate resulted in exchange of more than 95% Pu from 2N HNO_3, with less than 5% Np exchange.

Ferrous sulfamate reduction was the most promising method for extracting Np (IV) from a urine sample. When this procedure for Np is preceded by the U procedure, a good decontamination factor is obtained for each of the other actinides, with the exception of Th.

After removal of Np from the sample solution, the Pu (III) was oxidized by heating and addition of more HNO_3. The Pu (IV) and Pu (VI) were then exchanged to a separate solution of TIOA-xylene. Both Np and Pu were stripped from organic solution with distilled water.

Exchange with HDEHP

Slide 4 shows extractions with aqueous sample solutions and 20% HDEHP-toluene. More than 90% of the Th, Np, U, and Pu were exchanged from 4N HNO_3, and none of the Am or Cm was exchanged. By contrast, greater than 99% of the Am and Cm were exchanged from distilled water solutions (pH 4 - 5).

▶ AMERICIUM AND CURIUM

The urinary Am and Cm procedure is as follows (Slide 5). A sample is prepared in 4N HNO_3 and extracted into 20% HDEHP-toluene to remove Th, Np, U, and Pu. The aqueous solution is then neutralized with NH_4OH, and Am and Cm are exchanged to a fresh solution of HDEHP-toluene. Data in Slide 6 indicate that more than 95% Am was exchanged from a solution of oxidized urine when the equilibrium pH was between 3.7 and 5.1 (pH after extraction), and greater than 99% Am was exchanged at equilibrium pH 4.5. pH control is not critical enough to require instrument measurement for each sample, but can be satisfactorily achieved by adding consistent quantities of reagents. More than 95% of the Am and Cm present can be removed from solutions of urine in this way. Am and Cm were then stripped from the organic solution with 4N HNO_3. The acid was evaporated, and the residue was plancheted and counted.

Work in Progress

These liquid ion exchange procedures yield solutions suitable for electrodeposition of very small amounts of the actinides. Future work will include attempts to improve electrodeposition techniques so that detection limits will be lower than those possible by direct alpha counting.

References

1. Coleman, D. F., C. A., Blake, Jr., and K. B., Brown, Talanta 9, 297-323 (1962).

2. Schneider, R. A., Anal. Chem. 34, 522-525 (1962).

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1. SIX ACTINIDES EXTRACTED INTO 10% TIOA-XYLENE

AQUEOUS SOLUTION	PERCENT EXTRACTED					
	Th^{232}	Np^{237}	U^{238}	Pu^{239}	Am^{241}	Cm^{244}
DISTILLED H_2O (pH 4-5)					<10	0
HCl						
1N	<10	0	58	0		
2N	7	0	94	0	0	
3N	0	0	98	0		
4N	8	10	99	32	0	0
6N		33	100	19		
8N	0	95	100	39	0	
HNO_3						
4N	46	20	66	73	0	0

2. URANIUM-235 ANALYSIS OF 150 ml URINE

1.	WET OXIDATION	
2.	RESIDUE DISSOLUTION	50 ml 3.5N HCl.
3.	FIRST EXTRACTION	50 ml 10% TIOA-XYLENE - 2 MINUTES.
4.	SECOND EXTRACTION	25 ml 10% TIOA-XYLENE - 2 MINUTES.
5.	WASH	COMBINED TIOA (75 ml) WASHED WITH 15 ml 3.5N HCl; HCl DISCARDED.
6.	DESORPTION	TWO 25-ml DISTILLED H_2O WASHES OF TIOA-PHASE.
7.	PLANCHET AND COUNT	

3. FOUR ACTINIDES EXTRACTED INTO 10% TIOA-XYLENE FOLLOWING TREATMENT WITH VARIOUS REAGENTS

REAGENT	SOLUTION	PERCENT EXTRACTED Th	Np	U	Pu
AMMONIUM IODIDE	CONC HCl	35	>99	>99	<5
FERROUS AMMONIUM SULFATE	2N HNO_3	59	<5	22	>95
FERROUS SULFAMATE	4N HNO_3	15	>95	48	<3

4. SIX ACTINIDES EXTRACTED INTO 20% HDEHP-TOLUENE

AQUEOUS SOLUTION	PERCENT EXTRACTED Th^{232}	Np^{237}	U^{238}	Pu^{239}	Am^{241}	Cm^{244}
DISTILLED H_2O (pH 4-5)	67	43	60	72	>99	>99
HNO_3						
2N	35	66	>99	97	0	
4N	95	93	>99	90	0	0
8N	63	80	100	98	0	
HCl						
2N	52	0	>99	49	0	

5. AMERICIUM-CURIUM ANALYSIS OF 250 ml URINE

1.	WET OXIDATION	
2.	RESIDUE DISSOLUTION	50 ml 4N HNO_3.
3.	FIRST EXTRACTION	20% HDEHP-TOLUENE; DISCARD HDEHP.
4.	SECOND EXTRACTION	NEUTRALIZE AQUEOUS ABOVE WITH NH_4OH; EXTRACT WITH 20% HDEHP IN TOLUENE.
5.	WASH	HDEHP WASHED WITH 15 ml DISTILLED H_2O; WASH DISCARDED.
6.	DESORPTION	TWO 25-ml 4N HNO_3 WASHES OF HDEHP.
7.	PLANCHET AND COUNT	

6. AM^{241} FROM OXIDIZED URINE SOLUTION EXTRACTED INTO 20% HDEHP-TOLUENE