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ANALYSIS OF AMERICIUM IN TRANSPLUTONIUM PROCESS SOLUTIONS

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INTRODUCTION

One of the more difficult analyses in the transplutonium field is the determination of americium at trace levels in a complex matrix such as a process dissolver solution. These solutions have gross alpha and gamma radiations in the range of 10^{11} dis/(min)(ml) with accompanying high beta and neutron levels; alpha and gamma radiations contributed by americium are extremely small by comparison. Because of these conditions a highly selective separation must precede the measurement of americium. The separation technique should be mechanically simple to permit remote operation with master-slave manipulators. For subsequent americium measurement by the mass spectroscopic isotopic-dilution technique, plutonium and curium interferences must also have been removed.

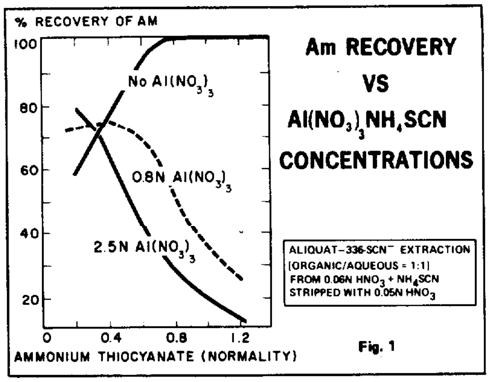
DISCUSSION and RESULTS

F. L. Moore's [1] method that uses "Aliquat-336-SCN$^-$" in xylene for the separation of actinides from lanthanides was modified to separate americium and curium from fission products, iron, mercury, aluminum and plutonium. Americium was separated from curium and californium by means of a potassium peroxydisulfate oxidation and HDEHP [di(2-ethylhexyl) -ortho-phosphoric acid] chromatographic column elution similar to the techniques of Moore [2] and Horwitz [3].

The two main variables affecting the extraction of americium at constant acidity (0.06 N HNO_3) by "Aliquat-336-SCN$^-$" /xylene are the concentrations of ammonium thiocyanate and aluminum nitrate in the aqueous phase (figure 1). The extraction of americium from solutions with low acid and without aluminum nitrate increases with increasing thiocyanate concentration. Figure 1 shows that aluminum nitrate suppresses the extraction of americium with increasing thiocyanate. This is of importance since high concentrations of aluminum nitrate are frequently encountered in process solutions. Because of this effect, an aqueous concentration of 0.44 N thiocyanate was selected for maximum americium recovery in process samples containing from 0 to 2.5 N aluminum nitrate.

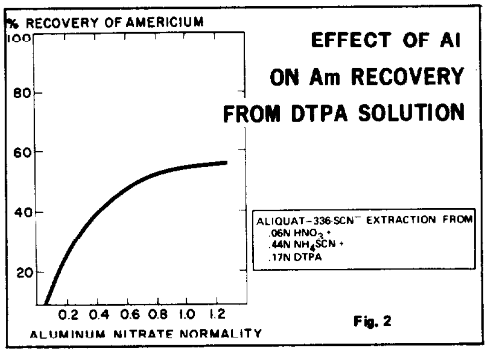
Americium recovery and decontamination factors are presented in table 1. Decontamination factors for the lanthanides from americium are the highest so far reported in the literature. To optimize the extraction of americium from the lanthanides and plutonium, the following steps were developed and evaluated:

1. An aqueous wash of the "Aliquat-336-SCN$^-$"/xylene phase with 0.44 N ammonium thiocyanate was performed.
2. The dilute nitric acid solution used to strip americium from the xylene phase was made 0.0002 N with sodium nitrite. This modification increased the plutonium decontamination factor from 8 to 100.



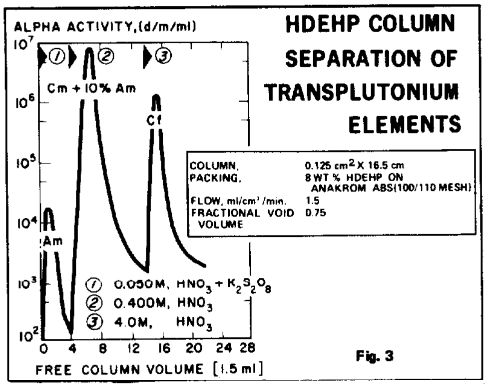
Am RECOVERY VS $Al(NO_3)_3$ NH_4SCN CONCENTRATIONS

Fig. 1



EFFECT OF Al ON Am RECOVERY FROM DTPA SOLUTION

Fig. 2



HDEHP COLUMN SEPARATION OF TRANSPLUTONIUM ELEMENTS

Fig. 3

Other elements normally encountered in process samples (iron, aluminum, mercury, zinc and fission products) were separated from americium to non-interfering levels.

Figure 2 shows that DTPA (diethylene-triaminepentaacetic acid) which is used in some processes to separate the transplutonium elements into individual species prevents the extraction of americium. It was found that the addition of aluminum nitrate to the samples prior to extraction eliminates the interfering effect of DTPA and makes unnecessary the time consuming sodium hydroxide precipitation of americium normally required in this type of sample.

Americium is separated from curium and californium on a chromatographic column of 8% HDEHP with inert diatomaceous earth support. Americium (III) is oxidized with solid potassium peroxydisulfate* to americium (VI) which self-reduces to americium (V). The nonsorbable americium (V) elutes rapidly in dilute acid, while curium (III) and californium (III) are held by the column. Curium can be separated from californium by increasing the nitric acid strength of the elutriant. The elution profile is shown in figure 3 and decontamination factors are given in table 2. For mass spectroscopic analysis americium is separated from neptunium and the sulfate salt of oxidation. This is accomplished by reduction with hydroxylamine nitrate and separation on another HDEHP column.

Table 1. Recovery & Decontamination of Americium

	One Extraction: 30% Am Recovery	Two Extractions + NH_4SCN Scrub: 17% Am Recovery
Decontamination Factors* for:		
Cerium	210	>1 × 10^5
Europium	29	>1 × 10^4
Zirconium	120	>2 × 10^3
Niobium	240	>2 × 10^3
Cesium	1400	>1 × 10^4
Ruthenium	120	>800
Plutonium	100	1 10^4
Iron	>2 × 10^3	>2 × 10^3
Mercury	>2 × 10^3	>2 × 10^3

* Corrected for Am recovery.

Table 2. Column Separation – Decontamination Factors & Recovery

Am Fraction		
DF:	Cm	>4 × 10^5
	Cf	>5 × 10^3
Am Recovery		90%
Cm Fraction		
DF:	Am	10
	Cf	>5 × 10^3
Cm Recovery		99%
Cf Fraction		
DF:	Am	>4 × 10^5
	Cm	4 × 10^3
Cf Recovery		99%

Table 3. Comparison of Americium Analyses

Sample	Concentration ^{243}Am, µg/ml Gamma Counting	Concentration ^{243}Am, µg/ml Mass Spectroscopic	Independent Analyses
Am-Cm Product (Deep Burn Pu)			
Sample 1	134	138.2	138
Sample 2	138	138.9	139
Pu Dissolv Soln (Deep Burn Pu)			
Sample 1	46.5	45.9	47.3
Sample 2	46.5	46.7	
*Pu Dissolv Soln (Cf Flowsheet)			
Sample 1	5.64	5.72	
Sample 2	5.43	5.69	5.59

* Sample radiation decreased from 7,500 to 17 mrad after aliquot 336-SCN$^-$ extraction and NH_4SCN scrub.

Results of the americium analyses are shown in table 3. The independent analyses were performed by a complex separation using fluoride, oxalate and hydroxide precipitations followed by high pressure chromatographic column separation.

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* The efficiency of oxidation of americium with solid potassium peroxydisulfate is normally 90%. When a freshly prepared solution of ammonium peroxydisulfate was used the oxidation was never more than 1%.

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