

**Short Communication**

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**MEASUREMENT OF TOTAL ALPHA-ACTIVITY  
OF NEPTUNIUM, PLUTONIUM AND AMERICIUM IN SIMULATED  
HANFORD WASTE BY IRON HYDROXIDE PRECIPITATION  
AND 2-HEPTANONE SOLVENT EXTRACTION**

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An improved method has been developed to concentrate the major  $\alpha$ -emitting actinide elements neptunium, plutonium, and americium from samples with high salt content such as those resulting from efforts to characterize Hanford storage tank waste. Actinide elements are concentrated by coprecipitation of their hydroxides using iron carrier. The iron is removed by extraction from 8M HCl with 2-heptanone. The actinide elements remain in the aqueous phase free from salts and iron. Recoveries averaged 98%.

The U.S. Environmental Protection Agency, the U.S. Department of Energy, and the Washington State Department of Ecology formed an agreement in May 1989, referred to as the Tri-Party Agreement, for the environmental restoration of the Hanford site in Southeastern Washington. This agreement requires the characterization of highly radioactive defense waste stored in 149 underground single-shell carbon steel tanks and 28 newer double-shell tanks. Characterization of the waste in the tanks is needed to select appropriate disposal methods. An important part of the characterization is the determination of the concentrations of the major  $\alpha$ -emitting actinide elements neptunium, plutonium, and americium in the waste. This determination requires that these individual elements be separated, purified, and measured. Before the separation, the total alpha activity of the  $\alpha$ -emitting radionuclides is measured. The total  $\alpha$ -activity measurement allows a determination to be made of the appropriate dilution factor to minimize radiation hazards associated with the separation processing.

The original procedure used to determine total  $\alpha$ -activity of Hanford waste samples had limitations. The procedure consists of drying an aliquot of the sample on a stainless steel planchet, baking the planchet on a hot plate to eliminate volatile salts and fix the activity, and then measuring the activity by proportional  $\alpha$ -counting. The procedure made no provision to remove highly radioactive, long-lived fission products such as

$^{137}\text{Cs}$ ,  $^{129}\text{I}$ ,  $^{99}\text{Tc}$  and  $^{90}\text{Sr}$  from the samples prior to  $\alpha$ -counting. The procedure was suitable only for samples in a non-corrosive (to stainless steel), nitric acid medium with a low salt concentration, otherwise self absorption attenuated  $\alpha$ -emissions and measurements were compromised. Dissolved Hanford waste samples are received for alpha activity measurements in a corrosive, hydrochloric acid medium with a high salt concentration. Hanford waste samples originally contain large quantities of inorganic salts, primarily of the alkali metals.<sup>1</sup> Hydrochloric acid and additional salt is introduced during sample dissolution by a molten-salt fusion method.<sup>2</sup>

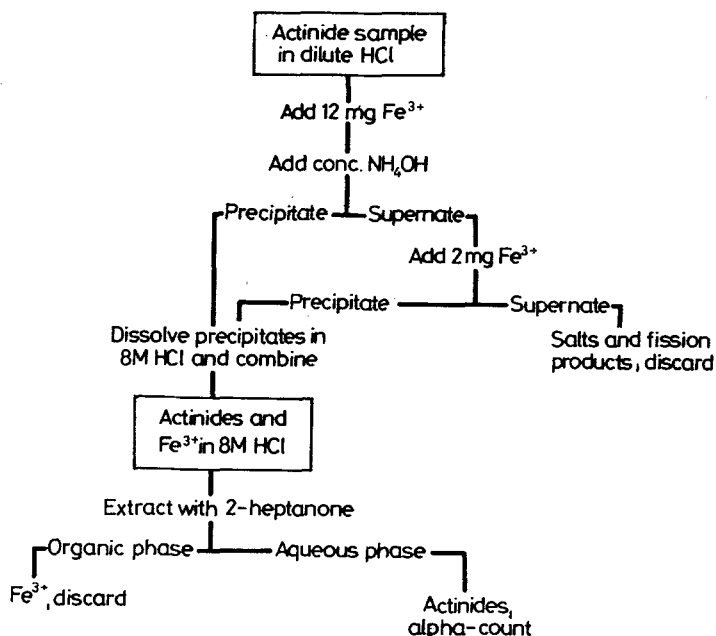
To overcome these limitations just described, a new procedure was developed in which the actinide elements are separated from long-lived fission products and salts and concentrated prior to  $\alpha$ -counting. The actinide elements are separated and concentrated by coprecipitation of their hydroxides using iron carrier, which is subsequently removed. Classically, iron carrier is removed by extraction from hydrochloric acid solution as chloroferric acid using ethyl or isopropyl ether. However, ethers tend to form peroxides that may reduce iron(III) to the iron(II) state, in which form it is no longer extractable. More importantly, peroxides present an unacceptable explosion hazard.<sup>3</sup> In the new procedure, these problems were avoided by selecting as an extractant 2-heptanone, a ketone that does not form peroxides.<sup>4</sup> Moreover, iron is extracted more efficiently by 2-heptanone than by ethers.<sup>5</sup>

## Experimental

*Chemicals and materials:* Chemicals used were ACS reagent grade. Because of the high level of radioactivity, labware used in this work was disposable. The iron carrier solution used in this work contained 10 mg of  $\text{Fe}^{3+}$ /ml and was prepared in 0.06M HCl.

*Samples:* Samples prepared for this work simulated dissolved Hanford waste. They contained known amounts of neptunium, plutonium and americium isotopes and potassium hydroxide and potassium nitrate acidified with hydrochloric acid. A mixture of potassium hydroxide and potassium nitrate is commonly used as the flux for the molten-salt fusion method employed for sample dissolution. Specifically, samples consisted of 1 ml of a 1.2M HCl solution containing nominally 100 Bq each of the isotopes  $^{237}\text{Np}$ ,  $^{239}\text{Pu}$  and  $^{241}\text{Am}$ , 10 mg of KOH and 2 mg of  $\text{KNO}_3$ . The  $^{237}\text{Np}$  and  $^{241}\text{Am}$  isotopes were obtained from Hanford stocks and the  $^{239}\text{Pu}$  isotope was obtained from Oak Ridge National Laboratory, Isotopes Division.

*Procedure:* The procedure is outlined in Fig. 1 and has been described in detail elsewhere.<sup>6</sup> The 1 ml sample aliquot was transferred to a 15 ml polypropylene screw-cap centrifuge tube after which 1 ml of deionized water and 1.2 ml of iron carrier solution (i.e., 12 mg  $\text{Fe}^{3+}$ ) were added and mixed. Concentrated ammonium hydroxide

Fig. 1. Separation of actinide elements for  $\alpha$ -counting

was added until the solution was distinctly basic causing iron to precipitate as a red-brown hydrated oxide which carried the actinide element isotopes. The centrifuge tube was capped, vortexed and allowed to digest overnight. It was convenient to carry out this coprecipitation at room temperature. Since the sample was not heated, overnight digestion was required for quantitative coprecipitation of the actinides. The solution was centrifuged and the supernate was transferred to a second centrifuge tube containing 0.2 ml of iron carrier solution (i.e., 2 mg Fe<sup>3+</sup>). The solution in the second centrifuge tube was vortexed and centrifuged, and the supernate was discarded as radioactive liquid waste. This second coprecipitation step scavenges any possible remaining actinides and thus further assures quantitative recoveries. The precipitates in both centrifuge tubes were dissolved in 8M HCl and the sample was recombined by quantitatively transferring the 8M HCl solution from the second centrifuge tube to the first. The second centrifuge tube was discarded as radioactive solid waste. The resulting volume of 8M HCl solution containing iron, neptunium, plutonium, and americium was about 2 ml. Iron(III) was successively extracted from the 8M HCl sample solution with 2–5 ml, followed by 1–4 ml volumes of 2-heptanone. The aqueous phase, now free of alkali metal and alkaline earth salts and iron carrier, was quantitatively transferred into a glass vial and

dried under a heat lamp. The dried sample was redissolved in 1M HNO<sub>3</sub> and an aliquot was deposited onto a stainless steel planchet. The planchet was dried under a heat lamp, baked on a hot plate, and the total alpha activity was measured by proportional alpha counting.

## Results

### *Coprecipitation*

An experiment was carried out to determine how much iron(III) carrier is needed to coprecipitate 90 percent or more of the actinides from a nominally 3 ml solution volume. Table 1 shows the percent  $\alpha$ -activity coprecipitated with iron(III) hydroxide,

Table 1  
Percent  $\alpha$ -activity coprecipitated with iron(III)  
carrier from 3 ml of solution

Fe <sup>3+</sup> added, mg	Alpha-activity coprecipitated, %
5	73
8	77
12	82
14	> 90

after an overnight digestion, as a function of the amount of iron(III) added. From the table it can be seen that ca. 14 mg of iron(III) is required to carry most of the alpha activity with the precipitate.

### *Iron extraction*

An experiment was conducted to test how efficiently iron(III) could be extracted from hydrochloric acid solution by 2-heptanone. In this experiment, 12 mg of iron(III) in 2 ml of 8M HCl was extracted twice with 4 ml of 2-heptanone. An aliquot of the aqueous phase turned red when tested with potassium thiocyanate, indicating the presence of iron. After another extraction with 4 ml of 2-heptanone, the thiocyanate test gave no color indicating that the aqueous phase was free of iron. Thus, three successive 4 ml volumes of 2-heptanone effectively extract iron carrier from a 2 ml volume of 8M HCl solution.

Table 2  
Recovery of total  $\alpha$ -activity of Np, Pu and Am

Sample	Recovery, %
1	96
2	98
3	98
4	99
5	97
Average:	$98 \pm 1$

### Recoveries

Based on the results of the above two experiments, five samples were processed using the procedure described in this paper. That is, 14 mg of iron(III) carrier was used in two successive steps and 14 ml of 2-heptanone extractant was used in three successive steps. Recoveries were high, averaging 98%, as is indicated in Table 2.

### Discussion

The experimental results support the efficacy of using ketone 2-heptanone instead of ethyl or isopropyl ether to extract iron. This extractant was selected because the distribution coefficient of 2-heptanone for iron(III) chloride is two orders of magnitude higher than that of the ethers under similar conditions.<sup>5</sup> Moreover, the hazards associated with the use of volatile ethers were avoided. In this procedure, the transposition of the 8M HCl aqueous phase to nitric acid prevented corrosion of the stainless steel planchet used for alpha counting. The actinide elements did not coextract with the iron(III) carrier and the aqueous phase containing the concentrated actinide elements was free of salts. In practice, this procedure eliminates the beta emitters, <sup>90</sup>Sr and <sup>99</sup>Tc, and gamma emitters, <sup>137</sup>Cs and <sup>129</sup>I. Thus, interference of alpha proportional counting by excessive beta activity, which is known to present problems,<sup>1</sup> is avoided and radiation hazards are minimized.

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