ION EXCHANGE SEPARATION AND MASS SPECTROMETRIC ANALYSIS OF URANIUM FOR SOLUTIONS CONTAINING PLUTONIUM

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ABSTRACT

An ion exchange technique separates plutonium from uranium using Dowex-1 resin and a methanol-HCl plutonium eluant. The method is applicable to both trace uranium determination and uranium isotopic distribution analysis by mass spectrometry. Distribution coefficients for plutonium, and elution curves for uranium and plutonium are shown. For uranium analysis the percent relative standard deviation is 0.8 at 120-2400 micrograms uranium per gram plutonium and 5.0 at 5 micrograms uranium per gram plutonium.
INTRODUCTION

A reliable method for uranium thorium separation using Dowex 1X8 strongly basic anion exchange resin and a HCl-methanol mixture has been reported by Korkisch and Tera. This investigation applied similar techniques to plutonium uranium separation so precise and sensitive uranium analysis in plutonium could be done using the isotopic dilution technique.

SUMMARY AND CONCLUSIONS

A new method has been developed for separating uranium from plutonium and has resulted in accurate and precise trace uranium analysis in plutonium. The method is applicable to plutonium dioxide, plutonium nitrate solutions and plutonium chloride solutions.

EXPERIMENTAL

MATERIALS

L-Ascorbic acid, reagent grade, was used to reduce Pu-IV and Pu-VI to Pu-III.

Dowex 1X8 (chloride form, 100-200 mesh) air dried was used in the investigation. Disposable polyethylene ion exchange columns were used (reservoir capacity = 25 ml, column outside diameter = 1.3 cm, column height = 8 cm, wall thickness = .2 cm).

Dow 50W (100-200 mesh) cation exchange resin was utilized to convert nitrate matrix to chloride matrix.

Methanol reagent grade
Standard Solutions

Uranium reference solutions 5 g/l, 1 g/l, .1 g/l, and .01 g/l were prepared by diluting by weight aliquots from a 400 g/l uranium solution characterized for uranium concentration gravimetrically.

Plutonium solutions with americium and uranium removed by ion exchange were characterized using alpha counting techniques.

Determination of Data for Elution Curves and Distribution Coefficients

Alpha counting was employed to determine plutonium and uranium data which was used to construct elution curves and distribution coefficients.

Distribution coefficients (Kd) were calculated using the equation:

\[
K_d = \frac{\mu g \text{ plutonium (uranium)/g resin}}{\mu g \text{ plutonium (uranium)/ul solution}}
\]

Uranium and plutonium distribution coefficients were determined by using 25 ml methanol-HCl mixtures, one gram Dowex 1X8 resin, and 24 hour shaking with an orbital shaker. Uranium and plutonium (5000 ug each) were determined from 2-5 ml samples taken from the resin-methanol-HCl mixture after allowing 4 hours for the resin to settle out of solution.

The determination of uranium to evaluate the reliability of the method was performed by thermal emission mass spectrometry using the equation:

\[
Cu = \frac{Cs \cdot Qs}{Qk} \cdot \frac{(Ws - Wm)}{(Wm - Wk)}^3
\]

where:

\[
Cu = \text{uranium concentration in sample}
\]

\[
Qs = \text{weight uranium in } ^{233}\text{U spike}
\]

\[
Qk = \text{weight plutonium or plutonium dioxide in sample}
\]
Ws = weight percent abundance of $^{233}$U in spike solution

Wm = weight percent abundance of $^{233}$U in mixture of sample plus spike

Wk = weight percent abundance of $^{233}$U in sample (Wk = 0 for most samples)

The uranium spike material isotopic abundance was greater than 99 percent $^{233}$U and was obtained from Oak Ridge National Laboratory

**Plutonium Valence Adjustment**

Plutonium trivalent solutions were obtained using L-ascorbic acid to reduce the Pu-VI and Pu-IV to Pu-III. Tetravalent plutonium solutions were obtained by adsorbing Pu-IV on strongly basic anion exchange resin, eluting Pu-III and Pu-VI with 4N HNO$_3$, and eluting Pu-IV with 0.5 N HNO$_3$.

**Nitrate to Chloride Matrix Conversion**

Plutonium nitrate solutions were converted to a chloride matrix by adjusting the hydrogen ion concentration to about 0.5 N, adsorbing the plutonium and uranium on Dow 50W cation exchange resin, washing the nitrate anion from the sample with deionized water, and eluting the uranium and part of the plutonium with 9N HCl. After matrix conversion the sample was ready for the plutonium uranium separation using Dowex 1X8 and methanol-HCl mixtures.

**RESULTS AND DISCUSSION**

Figure 1 is the elution curve for U-VI and Pu-III using 9N HCl and Dow 50W cation. The matrix conversion is complete in about one hour and greater than 50 percent of the plutonium is removed.

The distribution coefficients for uranium and plutonium, Figure 2, indicate the 90 percent methanol-10 percent 6N HCl mixture will yield
a clear-cut separation of uranium and tri-valent plutonium because their large distribution coefficient differences. The small volume of plutonium contaminated hydrochloric acid generated is an additional advantage in using the 90 percent methanol - 6N HCl plutonium elutriant.

There was no disagreement with the uranium distribution coefficients obtained and these reported by Korkisch and Tera.7

Because plutonium dioxide is dissolved using 9N HCl and 0.05 H HF, the effect 0.05 N HF on the distribution coefficients for U-VI, Pu-IV, and Pu-III was investigated. It was found that only tetravalent plutonium was affected by 0.05 N HF (Figure 3). The reaction:

\[ \text{Pu}^{4+} + \text{HF} \rightarrow \text{Pu}^{3+} + \text{H}^+ \quad \text{Keq} = (1.7 \times 10^6)^8 \]

explains the strong effect of 0.05N HF on the Kd of Pu-IV. Hence, relatively small quantities of fluoride improve the plutonium uranium separation if any tetravalent plutonium should be present.

Figure 4 is an elution curve indicating the separation and elution of plutonium and uranium using the 90 percent methanol-10 percent 6N HCl plutonium elutriant and 0.5N HCl uranium elutriant.

Column Operations

Dowex 1X8 anion exchange resin was equilibrated with 6N HCl and then transferred to a polyethylene exchange column. About 1-1/4 inches of the resin are added to the column. Methanol is added to the sample until an approximate 90 percent methanol - 10 percent sample mixture is obtained, then the resultant mixture is added to the reservoir of the polyethylene column. Two hundred ml 90 percent methanol - 10
percent 6N HCl solution is added to the column to assure plutonium removal. The uranium is eluted with 15 ml 0.5 N HCl. Figure 5 is a flow chart summary of the method.

Isotopic Dilution Results

One hundred microliters $^{233}$U spike solution were gravimetrically added to samples prior to uranium plutonium separation and uranium analysis. Table I indicates the precision of the method for high uranium concentrations ($U/Pu \sim 2$). Table II summarizes the effectiveness of the method for trace uranium analysis in plutonium (5 µg U/g Pu to 2500 µg U/g Pu).

REFERENCES

2. Ibid, page 532.
7. Korkisch and Tera, op. cit., p. 531
8. Wick, op. cit., p. 444.
FIGURE 3

Pu$^{IV}$

Pu$^{IV}$ - 0.05 N HF
10% 6N HCl - 93% Methanol

0.5N HCl

Pu

UVI

PERCENT ELEMENT ELUTED

MILLILITERS
<table>
<thead>
<tr>
<th>Sample</th>
<th>Pu g/l</th>
<th>#1</th>
<th>#2</th>
<th>Difference (1-2)</th>
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<tbody>
<tr>
<td>1</td>
<td>76.04</td>
<td>170.98</td>
<td>171.36</td>
<td>0.38</td>
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<td>2</td>
<td>76.43</td>
<td>171.05</td>
<td>171.96</td>
<td>0.91</td>
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<td>3</td>
<td>76.90</td>
<td>174.01</td>
<td>174.48</td>
<td>0.47</td>
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<td>4</td>
<td>76.87</td>
<td>173.74</td>
<td>171.37</td>
<td>2.37</td>
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<td>5</td>
<td>77.28</td>
<td>174.08</td>
<td>175.71</td>
<td>1.63</td>
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<td>174.08</td>
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<td>176.48</td>
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<td>9</td>
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<td>10</td>
<td>77.70</td>
<td>174.83</td>
<td>176.92</td>
<td>2.09</td>
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</tbody>
</table>

Average difference = 0.96
Percent relative standard deviation = 0.50
**TABLE II**

Data Table for Micrograms Uranium/gram Plutonium

<table>
<thead>
<tr>
<th>Sample #</th>
<th>µg U/g Pu Added</th>
<th>µg U/g Pu Found</th>
<th>% Recovery</th>
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<tr>
<td>1</td>
<td>4.985</td>
<td>4.835</td>
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<td>4.426</td>
<td>4.475</td>
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<td>3</td>
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<tr>
<td>11</td>
<td>2417.67</td>
<td>2413.7</td>
<td>99.84</td>
</tr>
</tbody>
</table>

Samples (1-3) (10 µl standard solution added)
Average percent recovery = 101.76
Percent relative standard deviation = 5.0

Samples (4-11) (90 µl - 240 µl standard solution added)
Average percent recovery = 100.21
Percent relative standard deviation = 0.83