HEAVY ELEMENT PROCESSING FLOW SHEET

EXTRACTION OF LANTHANIDES AND TRANSPLUTONIUM ACTINIDES INTO TRI-N-BUTYLPHOSPHATE (TBP) FROM A SOLUTION OF LOW ACIDITY WHICH IS HEAVILY SALTED WITH AI(NO₃)₃.

BACK-EXTRACTION OF THE LANTHANIDES AND ACTINIDES FROM TBP WITH H₂O.

EXTRACTION OF THE LANTHANIDES AND ACTINIDES FROM A DILUTE ACID SOLUTION WITH DI-2-ETHYLHEXYL ORTHOPHOSPHORIC ACID (HDEHP).

ESTERIFICATION OF THE HDEHP WITH DECANOL AND HCl, AND RECOVERY OF THE LANTHANIDES AND ACTINIDES IN THE AQUEOUS PHASE.

PASSAGE OF A CONCENTRATED HCl SOLUTION OF THE LANTHANIDES AND ACTINIDES THROUGH AN ANION EXCHANGE RESIN COLUMN.

ELUTION OF THE ACTINIDES FROM A CATION EXCHANGE RESIN COLUMN WITH A SATURATED HCl-ETHANOL SOLUTION.

Fig. 1
CONCENTRATION OF TRANSPLUTONIUM ACTINIDES FROM DIRT SAMPLES

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ABSTRACT OF THE DISCLOSURE

A method to concentrate the tripositive actinide elements produced in underground nuclear detonations in which the lanthanides and transplutonium actinides are extracted into tri-n-butylphosphate from large volumes of solutions of low acidity which are heavily salted with aluminum nitrate is described. The actinides and lanthanides are further extracted into tri-2-ethylhexyl orthophosphoric acid and are recovered in an aqueous phase after esterification with decanol. A concentrated hydrochloric acid solution of the actinides and lanthanides is passed through an anion exchange resin column. The actinides are then separated from the lanthanides by elution from a cation exchange resin column with a solution of ethanol-hydrochloric acid. A separation between the transcurium actinides and americium and curium is made on this column.

The invention described herein was made in the course of, or under a contract with the U.S. Atomic Energy Commission.

The method of this invention is used with 250 gram samples of earth which has been exposed to radiation by an underground nuclear detonation and can be scaled up to handle samples in the range of several kilograms. Contamination problems have plagued all earlier attempts to separate the actinides produced by underground nuclear detonations. In particular, the sample size of earlier procedures was limited to the 25-50 gram range, and such procedures were highly inefficient methods of obtaining significant recoveries of the actinides. This invention solves this problem of handling irradiated earth samples without the hazards involved previously.

The process of this invention involves the lanthanides and transplutonium actinides being extracted into tri-n-butylphosphate (TBP) from large volumes of solutions of low acidity which are heavily salted with aluminum nitrate. Following extraction, the TBP is scrubbed with ammonium nitrate solution and the lanthanide and actinide elements are back-extracted into water. To keep the volumes of TBP and water reasonably small, a relatively small volume of TBP is repeatedly brought into contact with small volumes of feed solution which reduces the yield of the product by about 10%. The actinides and lanthanides are extracted into tri-2-ethylhexyl orthophosphoric acid (HDEHP) from a solution of low acidity and are recovered in an aqueous phase after esterification of the HDEHP with decanol. Further decontamination is accomplished by passage of a concentrated hydrochloric acid solution of these elements through an anion exchange resin column. The actinides are then separated from the lanthanides by elution from a cation exchange resin column with an ethanol-hydrochloric acid solution. A separation between the transcurium actinides and americium-curiunm is made on this column. Although the procedure to be described in the preferred embodiment is written for samples weighing approximately 250 grams, the inventors have found that 2½ kilogram samples may be similarly processed without significant radiation hazard being encountered by using proportionately larger equipment and reagents.

It is therefore an object of this invention to provide a method of separating the transplutonium actinides from dirt samples obtained in a nuclear underground detonation and thus provide a process for obtaining the transplutonium actinides by a relatively inexpensive method.

A description of the preferred embodiment of this invention follows:

The ground-up sample is dissolved in a mixture of concentrated HNO₃, HClO₄, and HF, and boiled to fumes of HClO₄. At least three more additions of HF are made, with boiling to fumes of HClO₄ after each addition. The solution is made 4 M in HNO₃, then 4 M in HF, and the insoluble fluorides (including the tripositive actinide fluorides) are filtered. The precipitate is washed twice with 4 M HF–4 M HNO₃, dissolved in concentrated HClO₄, and diluted to make approximately 1200 milliliter of a solution of 1–2 M HClO₄.

Step 1

To the sample, add enough saturated Al(NO₃)₃ and 4 M LiOH to make the solution 1.7–1.9 M in Al(NO₃)₃ and about 0.1 M in H⁺ (pH 1). For a 1200-milliliter sample, this is generally accomplished by starting with a 600-milliliter portion in each of two 4-liter bottles. To each bottle add about 2000 milliliter of saturated Al(NO₃)₃ and then 4 M LiOH slowly from a dispensing buret while stirring the solution vigorously. Stop the addition of LiOH when the indicated pH is 0.9 to 1.1 (usually about 300 milliliter of LiOH). Adjust the Al(NO₃)₃ concentration up to 1.7–1.9 M (about three-fourths saturated).

Step 2

Pour 1 kilogram of TBP into the extraction vessel (see FIG. 2 for a picture of the extraction apparatus). Then add 500 milliliter of 1.9 M Al(NO₃)₃ and stir for 2 minutes. Draw off this pre-equilibrating Al(NO₃)₃ solution (the lower phase) and discard.

Step 3

By means of air pressure, force 500 milliliter of feed (the solution from Step 1) from a 4-liter bottle into the TBP transfer vessel. Drain the feed from the transfer vessel into the TBP in the extraction vessel. As soon as the addition of feed is begun, start the stirrer and continue stirring for 2 minutes. After the phases separate, drain the aqueous phase and discard. Repeat the procedure with successive 500-milliliter portions of feed; the total number of such contacts is not to exceed 18.

Step 4

Wash the TBP phase with one 500-milliliter portion of 1.9 M Al(NO₃)₃, stirring for 2 minutes, and then with five 500-milliliter portions of 10 M NH₄NO₃–0.2 M HNO₃, stirring for 5 minutes each time. Discard the washings.

Step 5

Back-extract the lanthanides and actinides with three 500-milliliter portions of H₂O, stirring for 2 minutes.
Concentrate the back-extracted sample to about 200-milliliters by boiling in an appropriate glass vessel or by using a rotary flash evaporator with a water-cooled condenser. The concentration step should be terminated before any material comes out of solution. Pass the concentrated solution through a filter to remove any remaining TBP.

To the concentrated solution, slowly add concentrated NH$_4$OH until a pH of 1.5–1.75 is reached. Transfer the solution directly to the HDEHP extraction vessel, add 200 milliliters of 0.5 M HDEHP in heptane, and stir for about 2 minutes. After the phases separate, drain the aqueous phase and discard. Wash the HDEHP phase with three 200-milliliter portions of 0.05 M HNO$_3$ drained from the transfer vessel into the extraction vessel. Discard the washings.

Drain the HDEHP phase into a 1-liter Erlenmeyer flask containing a magnetic stirring bar, and add 100 milliliters of decanol and 50 milliliters of concentrated HCl. Heat the washings.

Combine the desired fractions in a centrifuge tube and boil the solution almost to dryness. Add 2 milliliters of 0.05 M HNO$_3$ and heat if necessary to insure dissolution. Add 2 milliliters of 0.5 M HDEHP, stopper the tube, and shake for 2 minutes. Centrifuge briefly, and withdraw the aqueous (lower) phase and discard. Wash the organic phase with 2 milliliters of 0.05 M HNO$_3$ in a similar manner. Transfer the HDEHP to a 100-milliliter round-bottom flask containing a magnetic stirring bar, add 1 milliliter of decanol, 1 milliliter of concentrated HCl, and boil and stir for 15 minutes. Add 0.5 milliliter of concentrated HCl several times to insure the presence of an aqueous phase. Transfer the mixture to a centrifuge tube, centrifuge, and transfer the aqueous phase to a new centrifuge tube. To the HDEHP phase add 1 milliliter of 6 M HCl and shake. Centrifuge, draw off the aqueous phase, and combine it with the previous aqueous phase. Scrub the combined aqueous phase with 2 milliliters of heptane, centrifuge, and transfer the aqueous phase to a quartz or Vycor vessel. Boil the sample to dryness. Add a few drops of concentrated HNO$_3$ and concentrated HClO$_4$, and fume the sample dry again.

At this point, there is generally no visible material present. If there is any residue, a further separation can be performed by the precipitation of the actinides with NaOH in the presence of Fe(III) carrier. The iron is then removed on a small anion exchange resin column by a procedure like that described in Step 10. Another possible purification can be accomplished by absorbing the actinides on a small Dowex 50 cation exchange resin column from a solution 0.1 M in HCl, washing with the same acid, and stripping with 6 M HCl.

To facilitate the understanding of Step 3 above, one could treat each contact as an individual organic-aqueous system with an apparent distribution coefficient, K(e/a), between 20 and 40. With relative volumes of organic phase to aqueous phase of 2 to 1, between 97.5 and 98.8% of the actinides in the extraction vessel will be in the organic phase after each extraction. The following table shows how the overall yield would drop as a function of the number of extractions.

<table>
<thead>
<tr>
<th>Number of extractions</th>
<th>Percent Extracted (K=40)</th>
<th>Percent Extracted (K=20)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>99</td>
<td>98</td>
</tr>
<tr>
<td>5</td>
<td>99</td>
<td>98</td>
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<td>10</td>
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<td>15</td>
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<td>98</td>
</tr>
<tr>
<td>20</td>
<td>98</td>
<td>78</td>
</tr>
</tbody>
</table>

In fact, the distribution coefficient probably changes with the number of contacts. The TBP becomes more...
viscous, and phase separation times increase with the number of contacts.

A value of 20–40 for the apparent \( K \) is probably fairly representative of \( Y \). For \( \text{Nd} \), the value is between 10 and 20. In general, the value of \( K \) (and recovery) varies in the order:

\[ \text{Nd} < \text{Eu–Am} < \text{Y–Tb~Cf} < \text{Fm} \]

This difference might result in about a 10% fractionation of the actinides.

FIGURE 2 shows the TBP and the HDEHP extraction apparatus in which the lines to the aluminum nitrate, ammonium nitrate, and nitric acid wash solutions and also water are represented by 1; the TBP transfer vessel 2; the HDEHP transfer vessel 3; a typical solenoid valve 4; TBP mixing vessel 5; stainless steel centrifugal stirrer 6; HDEHP mixing vessel 7; Teflon gland 8; air pressure line 9; feed solution vessel 10; and vessels for receiving waste solutions or product 11.

SPECIAL EQUIPMENT
Extraction vessels (FIGURE 2): TBP vessels, 10 inches in length by 12.5 cm. O.D.; HDEHP vessel, 8 inches long by 9 cm. O.D.
Transfer vessels (FIGURE 2): TBP vessel, 8 inches long by 9 cm. O.D.; HDEHP vessel, 8 inches long by 7 cm. O.D.
Stainless steel centrifugal stirrers
Stirring motors
Teflon glands (source: Arthur F. Smith Co.)
Separatory funnels, with Teflon stopcocks
Bottles: 2 liter; 4 liter
pH meter with glass and calomel probes
Rotary flash evaporator, with a water-cooled condenser
Vacuum pump
Vinyl tubing
Teflon stopcocks
Solenoid valves
Switchbox for operating solenoid valves
Dispensing burets, with Teflon stopcocks
Glass columns for anion exchange resin: 8 cm. long by 10 mm. O.D.
Glass columns for cation exchange resin: 15 inches long by 9 mm. O.D.; with standard taper joint at top
Glass wool: used as plugs in all columns

SPECIAL REAGENTS USED IN PREFERRED EMBODIMENT
Saturated \( \text{Al(NO}_3\text{)}_3 \): Dissolve 5 lbs. of \( \text{Al(NO}_3\text{)}_3 \cdot 9\text{H}_2\text{O} \) in 1050 milliliters of \( \text{H}_2\text{O} \) to produce 2400 milliliters of solution. Heating speeds up the solution process.

1.9 \( \text{M Al(NO}_3\text{)}_3 \): 3 parts by volume of saturated \( \text{Al(NO}_3\text{)}_3 \) and 1 part of \( \text{H}_2\text{O} \)

10 \( \text{M NH}_4\text{–NO}_3 \): 0.2 M \( \text{HNO}_3 \): Dissolve 7 lbs. of \( \text{NH}_4\text{NO}_3 \) in \( \text{H}_2\text{O} \), add 50 milliliters of concentrated \( \text{HNO}_3 \), and dilute to 4 liters with \( \text{H}_2\text{O} \)

4 \( \text{M LiOH} \): Dissolve 671 grams of \( \text{LiOH} \cdot \text{H}_2\text{O} \) in \( \text{H}_2\text{O} \) and dilute to 4 liters

0.1 M \( \text{HCl} \) or \( \text{pH} \) 4 buffer for standardizing \( \text{pH} \) meter

Tri-n-butylphosphate (TBP)

0.5 M HDEHP: Dilute 645 grams of di-2-ethylhexyl orthophosphoric acid (94% purity) to 4 liters with n-heptane

Decanol

10 M \( \text{HCl} \)

0.05 M \( \text{HNO}_3 \)

\( \text{Te(IV)} \) carrier: 10 mg. \( \text{Te/ml.} \) (added as \( \text{Na}_2\text{TeO}_3 \) in 6 M \( \text{HCl} \))

\( \text{Te(VI)} \) carrier: 10 mg. \( \text{Te/ml.} \) (added as \( \text{Na}_2\text{TeO}_4 \cdot 2\text{H}_2\text{O} \) in 3 M \( \text{HCl} \))

\( \text{NH}_2\text{OH} \cdot \text{HCl} \): solid

n-Heptane

\( \text{EtOH} \cdot \text{HCl} \): 20% absolute ethanol—80% concentrated \( \text{HCl} \); saturated with \( \text{HCl} \) gas

Anion exchange resin: Bio-Rad Ag 1–X10, 100–200 mesh

Cation exchange resin: Bio-Rad Ag 50W–X4, minus 400 mesh (H+ form)

Concentrated \( \text{HCl} \)–38 weight percent hydrogen chloride in an aqueous solution

Concentrated \( \text{HF} \)–48 weight percent hydrogen fluoride in an aqueous solution

Concentrated \( \text{NH}_4\text{OH} \)–30 weight percent ammonia in an aqueous solution

Concentrated \( \text{HClO}_4 \)–71 weight percent perchloric acid in an aqueous solution

We claim:

1. A method of separating tripositive actinide and lanthanide elements from solutions of irradiated earth samples comprising, (a) extracting the actinide and lanthanide elements from a 1.9 molar \( \text{Al(NO}_3\text{)}_3 \) aqueous solution into tributyl phosphate and back-extracting with water, (b) extracting these elements into 0.5 molar di-2-ethylhexyl phosphoric acid, esterifying this acid solution with decanol, and back-extracting the lanthanide and actinide elements with concentrated \( \text{HCl} \), (c) passing a concentrated \( \text{HCl} \) solution of these elements through an anion exchange resin column, (d) precipitating hydroxides of these elements with 6 molar \( \text{NaOH} \) and with concentrated \( \text{NH}_4\text{OH} \), dissolving said hydroxides in concentrated \( \text{HCl} \), (e) separating the transcurium elements, americium-curium and the lanthanide elements by eluting from a cation exchange resin column with a solution of 20% absolute ethanol—80% concentrated \( \text{HCl} \) saturated with \( \text{HCl} \) gas.

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