Chemical Burnup Determination Based on Spectrophotometric Measurement of Total Rare Earth Fission Products, Uranium, and Plutonium

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CHEMICAL BURNUP DETERMINATION BASED ON SPECTROPHOTOMETRIC MEASUREMENT OF TOTAL RARE EARTH FISSION PRODUCTS, URANIUM, AND PLUTONIUM

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ABSTRACT

A chemical burnup procedure incorporates the ion-exchange separation of uranium, plutonium, and total rare earth fission products (as the fission monitor) followed by the spectrophotometric determination of each. The separation involves retaining uranyl and plutonyl chloride complexes on a macroporous anion exchange column from 12M HCl, whereas the rare earths and most fission products pass through. Subsequently, plutonium is eluted with 0.1M HI-12M HC1 and uranium with 0.1M HC1. From the initial effluent of the first column, the rare earth group is separated on a second column of either (1) macroporous anion exchange resin from HNO3-CH3OH, or (2) pellicular cation exchange particles from HCl-C2H5OH. The HNO3-CH3OH system normally is used to separate the rare earth group from fuel cladding elements and other fission products. The HCl-C2H5OH system additionally separates the rare earth group from americium. Arsenazo III is the chromogenic agent for the spectrophotometric determination of the separated uranium, plutonium, and rare earth fractions.

I. INTRODUCTION

Nuclear fuel burnup measurements are essential to both advanced fuel development studies and contemporary reactor operation evaluations. The most reliable technique for measuring burnup is based on destructive analyses for a selected fission product and for residual heavy atoms in a representative sample of the irradiated fuel. The computational relationship is

\[
\text{burnup} = \text{atom percent fission} = (100) \frac{\text{Number of fissions}}{\text{Initial number of heavy atoms}},
\]

and

\[
= (100) \frac{A/Y}{H + A/Y},
\]

where

\[
A = \text{determined atoms of fission monitor},
\]

\[
Y = \text{effective fission yield value of } A, \text{ and}
\]

\[
H = \text{determined residual heavy atoms}.
\]

The most sensitive and accurate technique for measuring burnup in fast breeder reactor (FBR) mixed-oxide fuels is based on the isotope dilution mass spectrometric measurement of \(^{148}\text{Nd}\), as the fission monitor, and uranium and plutonium, as
residual heavy atoms.\(^1\) The mass spectrometric procedure is capable of an overall burnup measurement precision of \(\leq 0.5\%\) relative standard deviation. Such a procedure\(^2\) was developed by our laboratory and is used routinely for analyzing experimental mixed-oxide fuels irradiated in EBR-II and other reactors.

Where such high precision is not warranted or where a mass spectrometer is not available, a less sophisticated burnup procedure using common, inexpensive chemical laboratory equipment would be of value. Such a procedure would determine a selected element or group of elements rather than a specific nuclide as the fission monitor and the residual uranium and plutonium.

Requirements for this procedure are that (1) selected fission monitor element(s) should have a high fission yield to allow high sensitivity without excessive radioactivity levels, (2) selected fission monitor(s) should have reasonably constant fission yields from the various contributing sources of fission, (3) high-sensitivity analytical techniques should be available for the selected element(s), and (4) ordinary low-cost laboratory instrumentation should be used.

The procedure described in this report is the first in a planned series to fulfill this need with emphasis on FBR-mixed uranium-plutonium fuels. It also is applicable to other fuel types.

### II. FISSION MONITOR SELECTION

Elemental zirconium and total rare earths (possibly including yttrium) are the two most promising fission monitor candidates for FBR mixed-oxide fuels. For reasons described below, we prefer the rare earths.

Postirradiation studies of experimental fast reactor mixed-oxide fuel show that only the rare earths’ (and possibly zirconium) fission products do not migrate axially relative to uranium and plutonium. Therefore, they are suitable to use as burnup monitors for these fuels.\(^1\)

Zirconium is produced in high abundance as shown in Table I. However, the zirconium fission yield varies substantially from one fissioning nuclide to another. Also, the aqueous chemistry of zirconium in a dissolved fuel solution is notoriously unpredictable.

The summed fission yield of total rare earths is higher than the zirconium fission yield and is more constant for different fissioning nuclides. Another advantage is that nuclear transmutations of rare earth isotopes by neutron capture or radioactive decay almost always produce another rare earth isotope. This provides constancy of fission yield independent of burnup level.

Chemical separation of the rare earth group is more difficult than the separation of zirconium, particularly if the trivalent actinides are to be excluded.

### TABLE I

**SUMMED FAST FISSION YIELDS FOR SELECTED FISSION PRODUCTS**

<table>
<thead>
<tr>
<th>Fissioning Nuclide</th>
<th>Zirconium(^a) (%)</th>
<th>Total Rare Earths (%)</th>
<th>Total Rare Earths Plus Yttrium (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>233U(^b)</td>
<td>32.8</td>
<td>45.6</td>
<td>51.4</td>
</tr>
<tr>
<td>235U(^b)</td>
<td>30.4</td>
<td>48.9</td>
<td>53.4</td>
</tr>
<tr>
<td>238U(^b)</td>
<td>26.0</td>
<td>47.7</td>
<td>50.3</td>
</tr>
<tr>
<td>239Pu(^b)</td>
<td>18.2</td>
<td>42.9</td>
<td>44.6</td>
</tr>
<tr>
<td>240Pu(^c)</td>
<td>18.0</td>
<td>47.1</td>
<td>48.7</td>
</tr>
<tr>
<td>241Pu(^c)</td>
<td>16.4</td>
<td>49.3</td>
<td>50.6</td>
</tr>
</tbody>
</table>

\(^a\)Assumes 2-yr irradiation and 2-yr cooling for \(^{90}\)Sr \(\beta \rightarrow ^{90}\)Zr.

\(^b\)Experimentally measured fission yields (Ref. 3).

\(^c\)Calculated fission yields (Ref. 4).
The chemical similarity of the trivalent actinides makes this group separation a challenge. Because of its greater applicability for FBR-mixed uranium-plutonium fuels, total rare earths was selected as the burnup monitor for this first chemical burnup procedure.

III. ANALYTICAL TECHNIQUE SELECTION

For this first procedure, the analytical technique selected was an ion exchange separation to provide fractions of plutonium, uranium, and total rare earths including yttrium, followed by a spectrophotometric measurement of each fraction using arsenazo III. Arsenazo III, first synthesized and studied extensively by Savvin, reacts with many metals to form highly stable, intensely colored complexes. This high stability enables complexes to be formed even in strong acid solution, thereby improving selectivity as well as avoiding problems of hydrolysis and polymerization. The molar absorptivities of the complexes for lanthanum through europium are very similar, a necessity because the proportions of the rare earth fission products differ as a function of the fissioning nuclide.

During this investigation, we found that commercially produced arsenazo III from various sources contained impurities that caused high blanks and erratic results. A simple purification procedure is described in Sec. VI.B.12.

IV. DISCUSSION OF ANALYTICAL PROCEDURE

A. Plutonium

Hydrofluoric acid and perchloric acid are added to a portion of the dissolved, irradiated fuel sample and then the mixture is fumed to dryness in Teflon or Kynar tubes. This treatment dissociates hydrolyzed forms of plutonium and oxidizes plutonium to (VI). Plutonyl and uranyl ions are strongly sorbed on a macroporous anion exchange resin column as complex chlorides from 12M HCl, whereas most other elements pass through. After flushing the nonsorbed ions from the column with 12M HCl, plutonium is reduced and eluted as nonsorbed Pu$^{3+}$ with 0.1M HCl-12M HCl at room temperature. Because the reduction of PuO$_2^+$ to Pu$^{3+}$ by iodide ion is not rapid, a 10-min delay after adding the HCl reagent provides complete reduction and elution of plutonium.

Plutonium (IV) forms exceptionally stable complexes with arsenazo III, even in strong acid media. Because plutonium is eluted from the column as Pu$^{3+}$, it must be converted to Pu$^{4+}$. The plutonium-containing eluate is evaporated to dryness and then fumed to dryness with HNO$_3$ to oxidize and expel all traces of iodide. The residue is dissolved in 6M HClO$_4$ and heated with H$_2$O$_2$ to convert all plutonium to Pu$^{4+}$. Excess peroxide, which would react with arsenazo III to cause bleaching of the complex (and unreacted chromogen), is destroyed with urea. The molar absorptivity of the Pu(IV)-arsenazo III complex in 6M HClO$_4$ is $1.4 \times 10^5$ at 665 nm.

B. Uranium

Uranium, not reduced by HI, remains sorbed on the anion exchange column when the plutonium is eluted. After the plutonium elution is complete, uranium is eluted with 0.1M HCl. The eluate is evaporated to dryness, the residue is fumed to dryness with HNO$_3$ to oxidize and expel the last traces of iodide, and the residue is dissolved in maleate-buffered hydrochloric acid.

The most intensely colored U(VI)-arsenazo III complex is formed at pH 1.7. At this pH, U(VI) forms only weak complexes with most aminocarboxylic acid chelating agents. N-(Carboxymethyl)-N'.2-hydroxyethyl-N, N'-ethylene-diglycine (HEDTA) therefore is incorporated in the buffer system to mask diverse cations that form arsenazo III complexes at this pH. The molar absorptivity of the U(VI)-arsenazo III complex under these conditions is $5.6 \times 10^4$ at 663 nm.

C. Total Rare Earths

The macroporous anion exchange separation from 12M HCl primarily removes uranium, plutonium, any iron from stainless steel fuel cladding, and fission products zirconium and antimony. A second ion exchange column is necessary to separate the rare earth group (plus yttrium) from other fission products, cladding components, and at times, trivalent actinides. Trivalent actinide elements, particularly americium, are chemically very similar to the rare earth elements. In plutonium-containing fuel with high $^{241}$Pu levels, the $^{241}$Am content may be great enough to bias the rare earth analysis. For such samples, a previously developed system is used to separate the rare earths from other elements,
including americium. In this system, americium and the rare earths are separated on a pellicular cation exchange particle column from a HCl-C2H5OH medium in which the stronger negative chloride complex of americium passes through. For fuels where the americium level will not significantly bias the rare earth measurement, a faster and less expensive second column of macroporous anion exchange resin is used to separate the rare earth-americium fraction from other elements in a HNO3-CH3OH medium.

The separated rare earth group is converted to an all-aqueous system at pH 2.9 and reacted with arsenazo III. Under these conditions, the rare earth (plus yttrium) fission products, in the proportions found in irradiated FBR mixed-oxide fuel with a U/Pu ratio of 3 in which uranium is 93% 235U, form an arsenazo III complex having a molar absorptivity of 4.8 x 10^4 at 665 nm.

V. TESTING AND PROCEDURE EVALUATION

The overall separation and spectrophotometric procedure was proof-tested by analyzing quadruplicate portions of six experimental mixed-oxide fuels [having a U/Pu ratio of 3 (in which uranium is 93% 235U)] that had been irradiated in EBR-II to burnup levels ranging from 2.7 to 11.2%. The spectrophotometrically determined burnup values are compared (Table II) to burnup values determined by the 148Nd isotope dilution mass spectrometric procedure. The relative standard deviation for an individual measurement by the spectrophotometric procedure was 4.8%. The mean value for four of the six fuels is not significantly different than the mass spectrometric burnup value, and the other two means are just significantly different by a "t" test at the 95% confidence level.

VI. APPARATUS AND REAGENTS

A. Ion Exchange Columns and Resins

1. Columns. Use 6-mm-i.d., 6-cm-long commercial polyethylene droppers (article No. 6219, Nalgene Company, Rochester, NY 14625, or equivalent) with a 2-mL reservoir for both macroporous anion exchange resin columns. Cut off the top of the dropper to form the reservoir, and place a small wad of quartz wool in the tip.

For the pellicular cation exchange resin, a 6-mm-i.d., 5-cm-long glass column is used. Because of the small particle size and consequent slow flow rate, a column designed to accept 0.034-atm (0.15-psig) air pressurization is recommended.

2. First-Column Resin. Transfer a water slurry of AGMP-1, 50- to 100-mesh, chloride-form resin (Bio-Rad Laboratories) to a polyethylene column until the settled height is just below the reservoir. Pass 6 mL of 12M HCl through the column. Keep the column wet with 12M HCl until use. (Do not prepare a column until a sample is ready.)

<table>
<thead>
<tr>
<th>Burnup Sample Designation</th>
<th>Mass Spectrometric Atom % Burnup</th>
<th>Spectrophotometric Atom % Burnup</th>
</tr>
</thead>
<tbody>
<tr>
<td>LASL-311</td>
<td>2.71</td>
<td>2.68 ± 0.18</td>
</tr>
<tr>
<td>LASL-329</td>
<td>5.52</td>
<td>5.78 ± 0.16</td>
</tr>
<tr>
<td>LASL-325</td>
<td>5.76</td>
<td>5.81 ± 0.25</td>
</tr>
<tr>
<td>LASL-302 J</td>
<td>6.04</td>
<td>5.86 ± 0.08</td>
</tr>
<tr>
<td>LASL-303 J</td>
<td>8.87</td>
<td>8.43 ± 0.59</td>
</tr>
<tr>
<td>LASL-223</td>
<td>11.24</td>
<td>10.75 ± 0.26</td>
</tr>
</tbody>
</table>

*Quoted uncertainties are standard deviations for a single determination computed from quadruplicate analyses.

a. Macroporous Anion Exchange Resin. Transfer a water slurry of AGM-1, 50- to 100-mesh, chloride-form resin (Bio-Rad Laboratories) to a polyethylene column until the settled height is just below the reservoir. Convert the resin to nitrate form by passing 10 m of 7.8M HNO₃ through each column. Then pass 6 m of 1.56M HNO₃-80° CH₃OH through the column just before loading the sample.

b. Pellicular Cation Exchange Resin. Transfer a HCl-C₂H₅OH (Reagent B,8) slurry of HC-Pellionex-SCX resin (H. Reeve Angel and Company) to a glass column until a resin bed height of 3.0 ± 0.2 cm is obtained. Pass through 2 m of HCl-C₂H₅OH to equilibrate the resin before loading the sample. New pellicular resin must be subjected to an entire sample loading-elution sequence (steps B.10 through B.15 of procedure in Sec. VII) to remove impurities before it is used for a sample.

B. Reagents

1. Hydrochloric Acid (12M, 6M, 0.1M). Quartz-distilled or other high-purity acid is recommended to minimize metal impurities. If quartz-distilled hydrochloric acid is used, the HCl gas lost during distillation must be replaced. This is accomplished by cooling the distilled acid and bubbling HCl gas through it until saturation is attained. Cooling in an ice bath is necessary because the reaction is exothermic. Verify that the HCl is at least 12M by titrating with standard NaOH solution to a phenolphthalein end point. (If the concentration is greater than 12M, dilution is recommended to avoid gas pocket formation in the columns.) Prepare 6M HCl by diluting 50 m of the 12M HCl to 100 m with quartz-distilled water. Prepare 0.1M HCl by diluting 1 m of the 12M HCl to 120 m with quartz-distilled water.

2. Hydriodic Acid-Hydrochloric Acid Mixture (0.1M HI-12M HCl). Dilute 1 m of distilled HI to 55 m with the purified 12M HCl. Prepare fresh reagent just before use. The HI is distilled, preferably in quartz apparatus, to remove H₂PO₃⁻, the holding reductant in analytical reagent (AR) grade HI. Store the distilled HI in flame-sealed ampoules under an inert atmosphere.

3. Hydrofluoric Acid (1M). Dilute 3 m of concentrated TransistAR grade HF or equivalent to 91 m with quartz-distilled water and store in a polyethylene dropping bottle.

4. Nitric Acid (15.6M, 7.8M, 1M). Use quartz-distilled or other high-purity HNO₃ for the 15.6M acid. Dilute 15.6M HNO₃ 1:1 with quartz-distilled water for the 7.8M HNO₃. Dilute 10 m of quartz-distilled HNO₃ to 156 m with quartz-distilled water for the 1M HNO₃.

5. Perchloric Acid (6M). Dilute 12M HClO₄ 1:1 with quartz-distilled water and store in a polyethylene dropping bottle.

6. Hydrogen Peroxide (30%). Refrigerate this AR solution when not in use.

7. 1.56 HNO₃-80% CH₃OH. Dilute 20 m of 7.8M HNO₃ to 100 m with AR grade anhydrous CH₃OH. Store the solution in quartz or borosilicate glass bottles with tight-fitting stoppers, preleached with HNO₃.

8. HCl-C₂H₅OH. Dilute 10 m of 12M HCl to volume in a 100-mL volumetric flask with anhydrous C₂H₅OH. Mix thoroughly, allow the solution to reach ambient temperature, and add more C₂H₅OH if necessary. Remove and discard 20 m of the solution with a pipet. Cool the flask containing the remaining 80 m of solution in an ice bath and bubble in HCl gas until the solution volume reaches 100 m. The HCl-C₂H₅OH reagent prepared in this manner is about 8M HCl as determined by NaOH titration. Store with a tight-fitting stopper. Prepare fresh after 3 days.

9. Maleate buffer, 0.5M maleic acid. 0.1 wt%. HEDTA, adjusted to pH 1.5 with NaOH.

10. Chloroacetate buffer, 1M. 0.015 wt%. HEDTA, adjusted to pH 2.9 with NaOH.

11. Urea, reagent crystals.

12. Arsenazo III solution. 0.055 wt%. Dissolve 550 mg of arsenazo III and 56 mg of NaOH in 900 m of quartz-distilled water. Stir until dissolution is complete. Prepare a 1.5- by 10-cm column of macroporous cation exchange resin, AGMP-50, 50-100 mesh (Bio Rad Laboratories). Wash the column with 200 m of quartz-distilled 7.8M HNO₃, then wash with water until the effluent is not less than pH 4. Pass the arsenazo III solution through this cation exchange column to remove metal impurities. Dilute the arsenazo III solution to 1000 m after the cation exchange purification.
C. Apparatus

1. Teflon beakers (5-mL, 15-mL).

2. Hot plate with hot air jets directed into the tubes to hasten sample evaporation.

3. Spectrophotometer must accommodate 1- and 5-cm pathlength cells.

4. Spectrophotometer cells, glass, 1-cm, 5-cm pathlength (semimicro style 5-cm cell with about 7-mL volume).

VII. ANALYTICAL PROCEDURE

A. Pretreatment

Add the sample, four drops of 6M HClO₄, and two drops of 1M HF to a 5-mL Teflon beaker. Evaporate to dryness using a hot plate and hot air jet. Redissolve the residue in five drops of 6M HCl and evaporate to about half this volume.

- The HF serves to dissociate polymerized species of plutonium. Fuming HClO₄ expels HF and oxidizes plutonium to Pu⁶⁺.

B. Chemical Separation

1. Transfer the pretreated sample to the first macroporous anion exchange column, prepared as described previously, with 0.5 mL of 12M HCl. Collect the effluent in a 15-mL Teflon beaker labeled “impure rare earth fraction.” Complete the sample transfer with another two 0.5-mL rinses of 12M HCl.

2. Pass 6 mL of 12M HCl through the column to completely elute the rare earth fraction.

- Americium and most fission products accompany the rare earths.

3. Place another 15-mL Teflon beaker labeled “plutonium fraction” under the column. Elute plutonium with 4 mL of 0.1M HI-12M HCl, followed by a 10-min wait, followed by another 6 mL of 0.1M HI-12M HCl.

- Iodide reduces plutonium to Pu³⁺, which is not sorbed from 12M HCl. The 10-min delay allows this reduction to go to completion.

4. Place another 15-mL Teflon beaker labeled “uranium fraction” under the column. Elute uranium with 6 mL of 0.1M HCl.

- Uranium does not form an anionic chloride complex in dilute HCl and is eluted.

5. Evaporate all three collected effluent fractions to dryness. Use very low heat initially to avoid overly vigorous gas release from the 12M HCl solutions.

- Alternatively, the 12M HCl solutions may be allowed to outgas in a hood overnight before heat is applied.

Note: If americium need not be separated from the rare earth fraction, do steps 6 through 9. If americium is to be separated, do steps 10 through 15.

6. Add 0.5 mL of 15.6M HNO₃ to the rare earth residue and evaporate to dryness. Dissolve the residue in 0.5 mL of 1M HNO₃, add three drops of H₂O₂, and again evaporate to dryness.

- The chloride salts are converted to nitrate salts. Ce⁴⁺ is reduced to Ce³⁺.

7. Prepare a second macroporous anion exchange resin column in HNO₃-CH₃OH as described previously. Dissolve the rare earth fraction residue (from step 6) in 0.5 mL of HNO₃-CH₃OH solution and transfer to the column. Repeat this transfer with another 0.5-mL portion, followed by a 1.0-mL portion of HNO₃-CH₃OH. Discard the effluent as contaminated waste solution.

- The rare earths (and americium) are sorbed on the column while other elements elute.

8. Pass another 5 mL of HNO₃-CH₃OH through the column. Discard the effluent as before.

- Elution of extraneous elements is completed.

9. Place a 15-mL Teflon beaker labeled “rare earth fraction” under the column. Elute the rare earth group with 6 mL of 1M HNO₃. Evaporate this solution to dryness. Dissolve the rare earth residue in 1 mL of 6M HCl and again evaporate to dryness. Proceed to part “C.”

- The rare earths do not form anionic nitrate complexes in aqueous HNO₃ and are eluted. Nitrate salts are converted to chloride salts.
10. Prepare a pellicular cation exchange resin column as described previously. Add 0.5 ml of C₂H₅OH-HCl solution to the rare earth residue from step 6, cover the Teflon beaker, and wait 10 min before loading this solution.

• The 10-min wait allows any Ce⁺⁺ to be reduced to Ce³⁺.

11. Transfer the dissolved rare earth fraction to the pellicular cation exchange resin column. Repeat this transfer with another 0.5-ml portion, followed by a 1.0-ml portion of HCl-C₂H₅OH. Pressurize the column with about 0.031 atm (0.5 psi) of air to obtain a flow rate of not less than 8 min/ml. Discard the effluent.

• The rare earths sorb while americium and many other elements elute.

12. Pass another 6 ml of HCl-C₂H₅OH through the column and discard this effluent also.

• The elution of americium is completed.

13. Pass 3 ml of water through the column, and more as necessary to elute any colored components from the column.

• An unidentified green component that sometimes sorbs from HCl-C₂H₅OH solution is eluted with water.

14. Place a 15-ml Teflon beaker labeled "pure rare earth fraction" under the column and elute the rare earths with 4 ml of 5M HCl. Evaporate this rare earth fraction to dryness.

15. Treat the pellicular cation exchange resin column with another 6 ml of 5M HCl, followed by 3 ml of water to ready it for reuse. (Note: Although pellicular cation exchange resin slowly degrades when used in strong acid, it has been reused satisfactorily 12 to 20 times.)

2. Dissolve the plutonium salt from the previous step in 3 ml of 6M HClO₄. Add 0.1 ml of 30% H₂O₂ and heat on a steam bath for 60 min.

• H₂O₂ converts all plutonium to Pu⁺⁺ in 6M HClO₄ medium.

3. Remove the Teflon beaker from the steam bath. Add 30 mg of urea, previously dissolved in 5 ml of 6M HClO₄, and heat for another 15 min.

• Urea destroys excess H₂O₂ that would bleach the Pu(III)-arsenazo III complex.

4. Pipet 5 ml of arsenazo III solution and 2 ml of 6M HClO₄ into a 25-ml volumetric flask. Mix by swirling. Quantitatively transfer the plutonium solution into the flask with three 2-ml portions of 6M HClO₄. Mix by swirling and wait 30 min.

5. Dilute the cooled solution to volume with 6M HClO₄ and mix thoroughly. Measure the absorbance vs 6M HClO₄ at 665 nm using 1-cm pathlength glass cells.

6. Compute the plutonium concentration from a four-point standard curve that brackets the absorbance region of the samples.

Note: If the sample absorbance is excessive, a dilution may be made with a diluent composed of 5 ml arsenazo III:20 ml 6M HClO₄.

D. Uranium Determination

1. Dissolve the uranium residue from step B.5 in 0.5 ml of 7.8M HNO₃ and evaporate to dryness. Add 0.5 ml of 6M HCl and again evaporate to dryness.

• Residual iodide that could interfere with color development is oxidized and expelled by HNO₃. The iodide-free uranium then is converted to a chloride salt.

2. Dissolve the uranium salt from the previous step in 3 ml of maleate buffer solution and heat for 30 min to ensure complete dissolution.

• HEDTA masks extraneous cations that form colored complexes with arsenazo III.

3. Quantitatively transfer the uranium solution to a 25-ml flask with three 3-ml water rinses. Add 3 ml of arsenazo III solution, mix thoroughly, and adjust the pH to 1.70 ± 0.02 with NaOH or HCl.
4. Dilute to volume with water and mix thoroughly. Measure the absorbance vs water at 663 nm using 1-cm pathlength cells.

5. Compute the uranium concentration from a four-point standard curve that brackets the absorbance region of the samples.

Note: If the sample absorbance is excessive, a dilution may be made with a diluent composed of 3 ml of malate buffer; 3 ml of arsenazo III; 19 ml of water.

E. Rare Earth Determination

1. Dissolve the rare earth residue from step B.9 (or B.14 if the pellicular cation exchange column was used) by adding 1 ml of chloroacetate buffer to the Teflon beaker and heating for 15 min.

2. Transfer the rare earth solution to a clean 10-ml volumetric flask with three 1-ml portions of water. Add 0.50 ml of arsenazo III solution, mix thoroughly, and adjust the pH to 2.90 ± 0.02 with NaOH or HCl.

3. Dilute to volume, mix thoroughly, and measure the absorbance vs water at 665 nm using 5-cm pathlength cells.

4. Compute the rare earth concentration from a four-point standard curve that brackets the absorbance region of the samples. Also compute the zero intercept from a least squares fit of the rare earth standard curve; use this as the blank value to be subtracted from each sample absorbance. (The composition of the rare earth standard solution is described in the Appendix.)

5. The burnup calculation is

\[
\text{atom percent burnup} = 100 \frac{\text{RE/FY}}{\text{U} + \text{Pu} + (\text{RE/FY})}
\]

where

\[
\text{RE} = \text{measured number of rare earth millimoles},
\]

\[
\text{FY} = \text{effective rare earth group fission yield}.
\]

\[
\text{U} = \text{measured number of uranium millimoles},
\]

\[
\text{Pu} = \text{measured number of plutonium millimoles}.
\]

REFERENCES


The composition of the rare earth solution used to prepare spectrophotometric standards should simulate the composition of rare earth fission products in the fuel sample being analyzed. Because many heavy nuclides may have fissioned, the fission yield for each mass chain from each fissioning nuclide must be considered when calculating the effective fission yield.

The calculation of an effective fission yield is illustrated in Table A-I for mass 141 for an experimental mixed-oxide fuel in which the U/Pu ratio is 3, the 235U enrichment is 93%, and the 240Pu level is 11%. This fuel had been irradiated in Row 1 of EBR-II.

Effective fission yields for mass chains 139 through 160, and 89 for yttrium, are calculated in a like manner. The values for each element are summed, and the relative elemental concentrations are computed. For the experimental fuel, the fission product rare earth composition computed and used as the spectrophotometric standard in this work was

<table>
<thead>
<tr>
<th>Element</th>
<th>Relative Moles</th>
</tr>
</thead>
<tbody>
<tr>
<td>La</td>
<td>0.125</td>
</tr>
<tr>
<td>Pr</td>
<td>0.110</td>
</tr>
<tr>
<td>Ce</td>
<td>0.271</td>
</tr>
<tr>
<td>Nd</td>
<td>0.324</td>
</tr>
<tr>
<td>Sm</td>
<td>0.080</td>
</tr>
<tr>
<td>Eu</td>
<td>0.006</td>
</tr>
<tr>
<td>Gd</td>
<td>0.002</td>
</tr>
<tr>
<td>Y</td>
<td>0.082</td>
</tr>
</tbody>
</table>

The final concentration of the rare earth mixture was determined by an EDTA titration to a xylene orange end point at pH 5.5 using pyridine buffer.

**TABLE A-I**

<table>
<thead>
<tr>
<th>Fissioning Nuclide</th>
<th>Preirradiated Fuel Composition Atom Fraction (AF)</th>
<th>Relative Fission Cross Section, $\sigma^b$</th>
<th>Fission Yield (FY)</th>
<th>Fractional Fission Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{235}$U</td>
<td>0.70</td>
<td>6.93</td>
<td>0.0585</td>
<td>0.0395</td>
</tr>
<tr>
<td>$^{238}$U</td>
<td>0.04</td>
<td>0.4</td>
<td>0.0531</td>
<td>0.00012</td>
</tr>
<tr>
<td>$^{239}$Pu</td>
<td>0.22</td>
<td>10.0</td>
<td>0.0515</td>
<td>0.0158</td>
</tr>
<tr>
<td>$^{240}$Pu</td>
<td>0.03</td>
<td>3.4</td>
<td>0.0486</td>
<td>0.00069</td>
</tr>
</tbody>
</table>

Fractional Fission Yield = \[\frac{[(AF)(\sigma)]}{\Sigma[(AF)(\sigma)]} \cdot \text{FY} \]

Effective Fission Yield = \[\sum \text{Fractional Fission Yield} = 0.0561 \text{ g} \]

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$^a$R. R. Heinrich, J. Williams, A. A. Madison, and N. D. Dudey, "Integral Measurements in EBR-II of Capture Rates, Fission Rates, and Alpha for $^{233}$U, $^{235}$U, $^{238}$U, $^{239}$Pu, $^{240}$Pu, and $^{242}$Pu," Argonne National Laboratory report ANL-7791 (July 1971).

