LA-6147

c.3

UC-79b
Reporting Date: October 1975
Issued: February 1976

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

by

S. F. Marsh
M. R. Ortiz
J. E. Rein

los alamos
scientific laboratory
of the University of California
LOS ALAMOS, NEW MEXICO 87545

UNITED STATES
ENERGY RESEARCH AND DEVELOPMENT ADMINISTRATION
CONTRACT W-7405-ENG. 36

This work was sponsored by the Fuels and Materials Branch of the Division of Reactor Development and Demonstration of the US Energy Research and Development Administration.

Printed in the United States of America. Available from
National Technical Information Service
U.S. Department of Commerce
5285 Port Royal Road
Springfield, VA 22151
Price: Printed Copy $4.50 Microfiche $2.25

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

by

S. F. Marsh, M. R. Ortiz, and J. E. Rein

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 12*M* HCl, whereas the rare earths and most fission products pass through. Subsequently, plutonium is eluted with 0.1*M* HI-12*M* HCl and uranium with 0.1*M* HCl. 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 HNO_3-CH_3OH, or (2) pellicular cation exchange particles from HCl-C_2H_5OH. The HNO_3-CH_3OH system normally is used to separate the rare earth group from fuel cladding elements and other fission products. The HCl-C_2H_5OH 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 = determined atoms of fission monitor,
Y = effective fission yield value of A, and
H = 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}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 ≤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/or 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

Fissioning Nuclide	Zirconium[a] (%)	Total Rare Earths (%)	Total Rare Earths Plus Yttrium (%)
^{233}U[b]	32.8	45.6	51.4
^{235}U[b]	30.4	48.9	53.4
^{238}U[b]	26.0	47.7	50.3
^{239}Pu[b]	18.2	42.9	44.6
^{240}Pu[c]	18.0	47.1	48.7
^{241}Pu[c]	16.4	49.3	50.6

---

[a] Assumes 2-yr irradiation and 2-yr cooling for $^{90}Sr \xrightarrow{\beta^-} {}^{90}Zr$.

[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,[5] 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 12*M* HCl, whereas most other elements pass through. After flushing the nonsorbed ions from the column with 12*M* HCl, plutonium is reduced and eluted as nonsorbed Pu^{3+} with 0.1*M* HI-12*M* HCl at room temperature. Because the reduction of PuO_2^{2+} to Pu^{3+} by iodide ion is not rapid, a 10-min delay after adding the HI-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 6*M* $HClO_4$ and heated with H_2O_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 6*M* $HClO_4$ is 1.4×10^5 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 0.1*M* 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 5.6×10^4 at 663 nm.

C. Total Rare Earths

The macroporous anion exchange separation from 12*M* 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[6] 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-C_2H_5OH 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 HNO_3-CH_3OH 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% ^{235}U, form an arsenazo III complex having a molar absorptivity of 4.8×10^4 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% ^{235}U)] 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 ^{148}Nd isotope dilution mass spectrometric procedure.[2] 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, Nalge 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[6] to accept 0.034-atm (0.15-psi) 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 12*M* HCl through the column. Keep the column wet with 12*M* HCl until use. (Do not prepare a column until a sample is ready.)

TABLE II

COMPARISON OF BURNUP VALUES DETERMINED BY SPECTROPHOTOMETRIC AND MASS SPECTROMETRIC PROCEDURES

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

---

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

3. Second-Column Resin.

a. Macroporous Anion Exchange 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. Convert the resin to nitrate form by passing 10 ml of 7.8*M* HNO_3 through each column. Then pass 6 ml of 1.56*M* HNO_3-80% CH_3OH through the column *just before loading the sample.*

b. Pellicular Cation Exchange Resin. Transfer a HCl-C_2H_5OH (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 ml of HCl-C_2H_5OH 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 (12*M*, 6*M*, 0.1*M*). 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 12*M* by titrating with standard NaOH solution to a phenolphthalein end point. (If the concentration is greater than 12*M*, dilution is recommended to avoid gas pocket formation in the columns.) Prepare 6*M* HCl by diluting 50 ml of the 12*M* HCl to 100 ml with quartz-distilled water. Prepare 0.1*M* HCl by diluting 1 ml of the 12*M* HCl to 120 ml with quartz-distilled water.

2. Hydriodic Acid-Hydrochloric Acid Mixture (0.1*M* HI-12*M* HCl). Dilute 1 ml of distilled HI to 55 ml with the purified 12*M* HCl. Prepare fresh reagent just before use. The HI is distilled, preferably in quartz apparatus, to remove H_3PO_2, the holding reductant in analytical reagent (AR) grade HI. Store the distilled HI in flame-sealed ampoules under an inert atmosphere.

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

4. Nitric Acid (15.6*M*, 7.8*M*, 1*M*). Use quartz-distilled or other high-purity HNO_3 for the 15.6*M* acid. Dilute 15.6*M* HNO_3 1:1 with quartz-distilled water for the 7.8*M* HNO_3. Dilute 10 ml of quartz-distilled HNO_3 to 156 ml with quartz-distilled water for the 1*M* HNO_3.

5. Perchloric Acid (6*M*). Dilute 12*M* $HClO_4$ 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 HNO_3-80% CH_3OH. Dilute 20 ml of 7.8*M* HNO_3 to 100 ml with AR grade anhydrous CH_3OH. Store the solution in quartz or borosilicate glass bottles with tight-fitting stoppers, preleached with HNO_3.

8. HCl-C_2H_5OH. Dilute 10 ml of 12*M* HCl to volume in a 100-ml volumetric flask with anhydrous C_2H_5OH. Mix thoroughly, allow the solution to reach ambient temperature, and add more C_2H_5OH if necessary. Remove and discard 20 ml of the solution with a pipet. Cool the flask containing the remaining 80 ml of solution in an ice bath and bubble in HCl gas until the solution volume reaches 100 ml. The HCl-C_2H_5OH reagent prepared in this manner is about 8*M* HCl as determined by NaOH titration. Store with a tight-fitting stopper. Prepare fresh after 3 days.

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

10. Chloroacetate buffer, 1*M*, 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 ml 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 ml of quartz-distilled 7.8*M* HNO_3, 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 ml 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 evaporations.

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 $6M$ $HClO_4$, 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 $HClO_4$ expels HF and oxidizes plutonium to Pu^{6+}.

B. Chemical Separation

1. Transfer the pretreated sample to the first macroporous anion exchange column, prepared as described previously, with 0.5 mℓ of 12 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 Pu^{3+}, 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 $15.6M$ HNO_3 to the rare earth residue and evaporate to dryness. Dissolve the residue in 0.5 mℓ of $1M$ HNO_3, add three drops of H_2O_2, and again evaporate to dryness.

- The chloride salts are converted to nitrate salts. Ce^{4+} is reduced to Ce^{3+}.

7. Prepare a second macroporous anion exchange resin column in HNO_3-CH_3OH as described previously. Dissolve the rare earth fraction residue (from step 6) in 0.5 mℓ of HNO_3-CH_3OH solution and transfer to the column. Repeat this transfer with another 0.5-mℓ portion, followed by a 1.0-mℓ portion of HNO_3-CH_3OH. 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 HNO_3-CH_3OH 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 $1M$ HNO_3. 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 HNO_3 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 C_2H_5OH-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^{4+} to be reduced to Ce^{3+}.

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-C_2H_5OH. Pressurize the column with about 0.034 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-C_2H_5OH 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-C_2H_5OH 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 5*M* HCl. Evaporate this rare earth fraction to dryness.

15. Treat the pellicular cation exchange resin column with another 6 mℓ of 5*M* 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.)*

C. Plutonium Determination

1. Dissolve the plutonium residue from step B.5 in 0.5 mℓ of 7.8*M* HNO_3 and evaporate to dryness. Add 0.5 mℓ of 6*M* HCl and again evaporate to dryness.

- Residual iodide that could interfere with color development is oxidized and expelled by HNO_3. The iodide-free plutonium then is converted to a chloride salt.

2. Dissolve the plutonium salt from the previous step in 3 mℓ of 6*M* $HClO_4$. Add 0.1 mℓ of 30% H_2O_2 and heat on a steam bath for 60 min.

- H_2O_2 converts all plutonium to Pu^{4+} in 6*M* $HClO_4$ medium.

3. Remove the Teflon beaker from the steam bath. Add 30 mg of urea, previously dissolved in 5 mℓ of 6*M* $HClO_4$, and heat for another 15 min.

- Urea destroys excess H_2O_2 that would bleach the Pu(III)-arsenazo III complex.

4. Pipet 5 mℓ of arsenazo III solution and 2 mℓ of 6*M* $HClO_4$ into a 25-mℓ volumetric flask. Mix by swirling. Quantitatively transfer the plutonium solution into the flask with three 2-mℓ portions of 6*M* $HClO_4$. Mix by swirling and wait 30 min.

5. Dilute the cooled solution to volume with 6*M* $HClO_4$ and mix thoroughly. Measure the absorbance vs 6*M* $HClO_4$ 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 $HClO_4$.

D. Uranium Determination

1. Dissolve the uranium residue from step B.5 in 0.5 mℓ of 7.8*M* HNO_3 and evaporate to dryness. Add 0.5 mℓ of 6*M* HCl and again evaporate to dryness.

- Residual iodide that could interfere with color development is oxidized and expelled by HNO_3. 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 maleate 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

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

where

RE = measured number of rare earth millimoles,
FY = effective rare earth group fission yield,*
U = measured number of uranium millimoles.

and

Pu = measured number of plutonium millimoles.

REFERENCES

1. W. J. Maeck, R. P. Larsen, and J. E. Rein, "Burnup Determination for Fast Reactor Fuels," US Atomic Energy Commission report TID-26209 (February 1973).

2. S. F. Marsh, M. R. Ortiz, R. M. Abernathey, and J. E. Rein, "Improved Two-Column Ion Exchange Separation of Plutonium, Uranium, and Neodymium in Mixed Uranium-Plutonium Fuels for Burnup Measurement, Los Alamos Scientific Laboratory report LA-5568 (June 1974).

3. W. J. Maeck, "Fast Reactor Fission Yields for U-233, U-235, U-238, Pu-239 and Recommendations for the Determination of Burnup on FBR Mixed-Oxide Fuels: An Interim Project Report," Allied Chemical Corporation report ICP-1050-1 (January 1975).

4. E. W. Sidebotham, "Fission Product Yield Data Extrapolated for Some Actinides," United Kingdom Atomic Energy Authority report TRG-Report-2143(R) (1972).

5. S. B. Savvin, "Arsenazo III: Methods of Photometric Determination of Actinide Elements," (Moska Atomizdat, 1966) English translation FTD-HT-23-67-68 by Translation Division, Foreign Technology Division, Wright Patterson AFB, OH (1968).

6. S. F. Marsh, M. R. Ortiz, and J. E. Rein, "Cation Exchange Behavior of Lanthanides and Trivalent Actinides in Ethanol-Hydrochloric Acid," Los Alamos Scientific Laboratory report LA-5728 (December 1974).

---

*The calculation of an effective fission yield is described in the Appendix.

APPENDIX

CALCULATION OF EFFECTIVE FISSION YIELD AND PREPARATION OF RARE EARTH STANDARDS

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 ^{235}U enrichment is 93%, and the ^{240}Pu 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

Element	Relative Moles
La	0.125
Pr	0.110
Ce	0.271
Nd	0.324
Sm	0.080
Eu	0.006
Gd	0.002
Y	0.082

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

TABLE A-I

COMPUTATION OF EFFECTIVE FISSION YIELD

Fissioning Nuclide	Preirradiated Fuel Composition Atom Fraction (AF)	Relative Fission Cross Section, σ_f[a]	Fission Yield (FY)	Fractional Fission Yield
^{235}U	0.70	6.93	0.0585[b]	0.03958
^{238}U	0.04	0.4	0.0531[b]	0.00012
^{239}Pu	0.22	10.0	0.0515[b]	0.01580
^{240}Pu	0.03	3.4	0.0486[c]	0.00069

$$\text{Fractional Fission Yield} = \frac{[(AF)(\sigma_f)]}{\Sigma[(AF)(\sigma_f)]}\,[FY]\ .$$

$$\text{Effective Fission Yield} = \Sigma\ \text{Fractional Fission Yield} = 0.0561_9 .$$

---

[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).

[b] W. J. Maeck, "Fast Reactor Fission Yields for U-233, U-235, Pu-239 and Recommendations for the Determination of Burnup on FBR Mixed-Oxide Fuels: An Interim Project Report," Allied Chemical Corporation report ICP-1050-1 (January 1975).

[c] E. W. Sidebotham, "Fission Product Yield Data Extrapolated for Some Actinides," United Kingdom Atomic Energy Authority report TRG-Report-2143(R) (1972).