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DISSOLVED ORALLOY STANDARDS AND THE ORIGIN OF HEU

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I. INTRODUCTION

One of the questions that the Nuclear Chemistry Division's Attribution program would like to be able to answer is: Where did this sample of special nuclear material come from? The Plutonium Origins project is trying to develop techniques to answer this question for a sample of plutonium. The ingrowth of daughter activities defines the date when the material was chemically processed; the plutonium isotopics define the enrichment of uranium and the neutron spectrum in the reactor target, and residual impurities in the sample identify the chemical techniques used in reprocessing.

The forensic signatures in a sample of highly-enriched uranium (HEU) are different. While ingrowth of daughter activities can still be used to define a separation time, the material need not ever have been resident in a reactor, and residual impurities are very effectively removed by the mass enrichment process. Nevertheless, the sample can be examined for the synthetic uranium isotopes (e.g. ^{232}U , ^{233}U , and ^{236}U), whose presence would indicate the use of irradiated uranium in the feed material at some point in the history of the cascade. We can also look for other heavy-element contaminants, that might have been introduced into the material in the post-cascade processing into refined metal.

This report describes an analytical procedure for use in determining the heavy element content of a sample of HEU. The results of the analysis of a specific sample are discussed and some forensic signatures are identified. Two calibrated liquid samples were created, containing known amounts of HEU and contaminants. These samples were counted for gamma rays in the same way that an HEU sample would be treated, and the results of the gamma counting are compared with the analytical results.

II. RADIOCHEMICAL ANALYSIS AND COUNTING

A sample of Oralloy (U.S. standard HEU) foil was obtained from B-151, where it had been stored for more than ten years. The foil was heavily oxidized; it was not cleaned prior to these analyses. A circular piece of the sample 1.21-inches in diameter and weighing 3.3-g was cut out with a pair of scissors and mounted in a plastic gamma-spec holder sealed with several layers of scotch tape. The total

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thickness of plastic covering the sample was 0.12 g/cm^2 water-equivalent. This sealed source was counted for gamma rays in both the B-151 counting facility (at a detector-sample distance of 10 cm, for 2 to 3 days in each of two detectors) and in B-251 with a Safeguards system. The sample was then dissolved in a 50 ml beaker with hot 8M HNO_3 . The resulting solution was kept warm for 20 hours, then was transferred quantitatively to a 10-ml volumetric flask with several 8M HNO_3 washes of the gamma-spec holder and glassware. The empty glassware, empty gamma-spec holder, and surrounding hood paper were packed into a 1-pint ice-cream carton and counted for gamma rays; only $(880 \pm 60) \text{ dpm } ^{235}\text{U}$ ($\sim 0.18 \text{ mg}$, or 0.005%) was lost in the transfer.

Volumetric glassware was calibrated by weight with recently-boiled water or with mercury. An aliquot containing 6 ml of the Oralloy stock solution was transferred to a gamma-spec "Prindle vial", and diluted to 10.0 ml with 8M HNO_3 . The total weight of the solution was 14.9 g. A second aliquot containing 2 ml of the Oralloy stock solution was transferred to another Prindle vial and diluted to 10.0 ml with 8M HNO_3 . The total weight of this solution was 13.3 g. Both Prindle vials were sealed with Dow 732 RTV sealant and were then placed in larger vials, which were similarly sealed. The combination of 10 ml of solution in the two nested vials is a standard counting geometry for the B-151 counting facility. Both samples were counted for gamma rays with down-looking detector U5. The detector-to-sample distance was 8.6 cm; the lids of the nested Prindle vials were a total of 0.36 g/cm^2 water-equivalent in thickness. Each solution was counted for 30 to 60 minutes without additional absorbers, and for 3 to 4 days with 1.36 g/cm^2 Cd and 0.964 g/cm^2 Pb absorbers placed between the sample and the detector.

The procedure used in the radiochemical analysis and standardization of small aliquots of the Oralloy stock solution is given in the Appendix.

Results of the radiochemical analysis of the Oralloy sample are given in Table I, in atoms/milliliter of stock solution, decay corrected to day 237, 1993. It should be emphasized that these data were obtained from analytical samples containing only 160 mg each of the original material; larger samples could result in higher-quality information on minor element components. Comparison of results obtained from different analytical samples gave no evidence of cross-contamination or environmental contamination. The nuclide contents of the strong and weak dilutions of the stock solution, sealed in double Prindle vials to form our solution standards, can be obtained by multiplying the Table I data by $(5.9713 \pm 0.0095) \text{ ml}$ and $(1.9984 \pm 0.0031) \text{ ml}$, respectively, and correcting for radioactive decay from the reference time.

III. SIGNATURES

TABLE I. RADIOCHEMICAL ANALYSIS OF AN ORALLOY SAMPLE, IN ATOMS/MILLILITER OF STOCK SOLUTION, DECAY CORRECTED TO DAY 237, 1993.

<u>NUCLIDE</u>	<u>ATOMS/ML</u>	<u>NUCLIDE</u>	<u>ATOMS/ML</u>
^{243}Am	$\leq 1.6 \times 10^9$	^{235}U	$(7.595 \pm .082) \times 10^{20}$
^{241}Am	$(1.446 \pm .006) \times 10^{11}$	^{234}U	$(8.170 \pm .088) \times 10^{18}$
^{242}Pu	$(2.914 \pm .032) \times 10^{11}$	^{233}U	$(1.144 \pm .084) \times 10^{15}$
^{241}Pu	$(6.551 \pm .088) \times 10^{10}$	^{232}U	$(1.94 \pm .42) \times 10^{11}$
^{240}Pu	$(3.170 \pm .032) \times 10^{12}$	^{231}Pa	$(2.042 \pm .046) \times 10^{13}$
^{239}Pu	$(5.194 \pm .052) \times 10^{13}$	^{232}Th	$\leq 1.4 \times 10^{16}$
^{238}Pu	$(4.607 \pm .046) \times 10^{11}$	^{230}Th	$(4.54 \pm .15) \times 10^{14}$
^{236}Pu	$\leq 4.8 \times 10^6$	^{229}Th	$(9.82 \pm .81) \times 10^{10}$
^{237}Np	$(1.271 \pm .056) \times 10^{15}$	^{228}Th	$(5.27 \pm .17) \times 10^9$
^{238}U	$(4.389 \pm .048) \times 10^{19}$	^{227}Ac	$(3.94 \pm .36) \times 10^9$
^{236}U	$(3.615 \pm .038) \times 10^{18}$	^{226}Ra	$(3.94 \pm .15) \times 10^{10}$

Table I includes the concentrations of several nuclides that are linked by radioactive decay. For instance, ^{234}U decays to ^{230}Th with a half life of 2.446×10^5 years; in turn, ^{230}Th decays to ^{226}Ra with a half life of 7.54×10^4 years. If one makes the assumption that at some time all Th was removed from the sample, the relative amounts of ^{234}U and ^{230}Th at the analysis time define the sample's age (the amount of time that has passed since the separation took place). Similarly, the relative amounts of ^{234}U and ^{226}Ra provide an independent measure of the age of the sample, assuming that Ra and Th were removed at the same time. Table II gives several independent determinations of the apparent age of the sample, extracted from the concentrations of the indicated nuclide pairs. Because of the short half life of ^{228}Th (1.9 years), the $^{232}\text{U}/^{228}\text{Th}$ pair is of limited use in determining ages of more than six years. The range of ages represented by the values in Table II far exceeds the errors associated with the measurements. This is a result of the incomplete removal of the daughter nuclides in the chemical processing, or their introduction into the sample at some later time.

TABLE II. AGE OF THE ORALLOY SAMPLE ON DAY 237, 1993, AS DETERMINED FROM SEVERAL DIFFERENT RADIOGENETIC RELATIONSHIPS.

<u>NUCLIDE PAIR</u>	<u>APPARENT AGE (YEARS)</u>
$^{232}\text{U} - ^{228}\text{Th}$	> 5.0
$^{235}\text{U} - ^{231}\text{Pa}$	27.32 ± 0.91
$^{235}\text{U} - ^{227}\text{Ac}$	25.30 ± 1.46
$^{234}\text{U} - ^{230}\text{Th}$	19.62 ± 0.86
$^{234}\text{U} - ^{226}\text{Ra}$	19.27 ± 0.47
$^{241}\text{Pu} - ^{241}\text{Am}$	24.46 ± 0.26

One interpretation of the data in Tables I and II is: From the ^{234}U ages, the material was cleaned of thorium and radium sometime between Nov. 21, 1973, and Sep. 9, 1974 (one sigma). A chemical separation which successfully removes Th and Ra from uranium will likely also remove actinium, but might not remove protactinium. If one assumes that only Pa was left in the sample at $t_0 - (19.35 \pm 0.41)$ years, the residual ^{231}Pa and ^{227}Ac activities define an age of 16.4 ± 6.8 years before analysis time, which is consistent with the ages determined from the ^{234}U decay chain. The amount of residual Pa is consistent with at least 7.13 years of ingrowth prior to the Th, Ac, and Ra separations. This assumes that no ^{231}Pa was removed from the sample in the final processing; if some Pa was removed, this time becomes longer. Therefore, the enriched material had to have existed prior to 1967, but was not purified for the last time until 1974.

The presence of ^{232}U , ^{233}U , and ^{236}U in the sample proves that the enrichment cascade had been contaminated with reactor-irradiated uranium. The values of $^{232}\text{U}/^{235}\text{U}$ and $^{233}\text{U}/^{236}\text{U}$ are probably unique to a given batch of material. Neptunium, plutonium, and americium are uranium irradiation products, but are highly unlikely to pass through the enrichment cascade with the low-mass uranium cut, even though both Np and Pu have volatile hexafluorides. The presence of ^{237}Np in the sample could be due to 6.75-day ^{237}U in the feed material, implying the use of freshly-irradiated uranium in the cascade; however, it seems more likely that the Np, Pu, and Am contents are due to contamination after the mass enrichment. The age defined by the $^{241}\text{Pu}/^{241}\text{Am}$ pair is particularly revealing. Any Am must have been removed from the uranium sample at the time that Ac was removed because of their similar chemical properties. Since the $^{241}\text{Pu}/^{241}\text{Am}$ age is significantly older than that of the other separation, the plutonium was not present in the sample when it was purified. The sample was contaminated with Pu, which had last been cleaned of Am in early 1969, during one of the metallurgical processes (e.g., in the rolling of the Oralloy ingot into foil).

The nuclide content of the stock solution, corrected for 19.35 ± 0.41 years of decay, is given in Table III. Relative plutonium and uranium isotopics are given in parentheses. The value of $^{240}\text{Pu}/^{239}\text{Pu}$ is consistent with weapons-grade plutonium, though the relative amounts of ^{242}Pu and ^{238}Pu are higher than one would expect for U.S. material. Some of the ^{238}Pu excess may have been introduced with the ^{237}Np contamination; massive samples of neptunium often contain more than 100 ppm ^{238}Pu .

TABLE III. NUCLIDE CONTENT OF 1.0 ML OF STOCK SOLUTION, DECAY CORRECTED TO DAY 109, 1974 (± 150 DAYS). RELATIVE ISOTOPICS OF PLUTONIUM AND URANIUM COMPONENTS ARE INDICATED IN PARENTHESES. THE RELATIVE ^{241}Pu ISOTOPIC INCLUDES THE ^{241}Am CONTENT.

NUCLIDE	ATOMS/ML	NUCLIDE	ATOMS/ML
^{241}Am	$(4.65 \pm .20) \times 10^{10}$	^{238}U	$(4.389 \pm .048) \times 10^{19} (5.38\%)$
^{242}Pu	$(2.914 \pm .032) \times 10^{11} (0.52\%)$	^{236}U	$(3.615 \pm .038) \times 10^{18} (0.44\%)$
^{241}Pu	$(1.67 \pm .03) \times 10^{11} (0.38\%)$	^{235}U	$(7.595 \pm .082) \times 10^{20} (93.17\%)$
^{240}Pu	$(3.176 \pm .032) \times 10^{12} (5.65\%)$	^{234}U	$(8.170 \pm .088) \times 10^{18} (1.00\%)$
^{239}Pu	$(5.197 \pm .052) \times 10^{13} (92.49\%)$	^{233}U	$(1.144 \pm .084) \times 10^{15}$
^{238}Pu	$(5.368 \pm .056) \times 10^{11} (0.96\%)$	^{232}U	$(2.36 \pm .51) \times 10^{11}$
^{237}Np	$(1.271 \pm .056) \times 10^{15}$	^{231}Pa	$(5.94 \pm .55) \times 10^{12}$

The absolute contaminant levels of the sample immediately after processing (assuming metallurgical processing closely followed the last chemical purification step) were 70.1 ± 1.0 ppb (parts per 10^9) of plutonium, 1570 ± 70 ppb of neptunium, and 7.2 ± 0.7 ppb of protactinium. These contaminants, along with the >7-year span that the enriched material existed prior to the last chemical separation, imply that the foil was produced in a plant with several different functions, not necessarily all weapons-related (^{237}Np), one of which involved the re-use of old HEU parts.

IV. COMPARISON OF ANALYTICAL DATA WITH COUNTING DATA.

Even though the radiochemical technique is powerful, it is labor intensive and time consuming (see Appendix). Consequently, we would also like to develop a technique for non-destructive determination of forensic information in HEU through the counting of gamma rays. Besides the obvious problem of being insensitive to low-intensity gamma rays in the presence of higher activities, this technique suffers from another limitation: The intrinsic activities of most of the uranium isotopes and their decay daughters are very low because of their long half lives. This requires large counting samples in order to have reasonable decay rates for minor components in the materials. The self-absorption of low-energy photons is quite severe; for instance, given a piece of HEU 1-cm thick, only 3.6% of the 186-keV photons (54% of ^{235}U decays) emitted normal to the surface leave the material unchanged. If samples are inhomogeneous or poorly-characterized in shape, a quantitative analysis is virtually impossible. Counting the uranium in a gaseous or liquid form (e.g. UF_6) does ensure sample uniformity, but doesn't help with the absorption problem, since the photon half-thickness of the source is a function of mass thickness (grams/cm²) rather than density.

Table IV compares the results of gamma counting the original metal foil sample on two detectors in the B-151 counting facility with the results of the analytical procedure (Table I), scaled to the size of the original sample. Photons with energies of less than 100 keV were not used in the analysis. For most of those nuclides that could be observed through their gamma-ray emissions, agreement between the

TABLE IV. COMPARISON OF ANALYTICAL DATA WITH COUNTS OF THE UNDISSOLVED METAL FOIL.

<u>NUCLIDE</u>	<u>DPM SCALED ANALYTICAL</u>	<u>DPM, DET U5</u>	<u>DPM, DET X3</u>
$^{234\text{m}}\text{Pa}(^{238}\text{U})$	$(1.29 \pm .02) \times 10^5$	$(1.87 \pm .26) \times 10^5$	$(1.88 \pm .27) \times 10^5$
$^{234\text{g}}\text{Pa}(^{238}\text{U})$	$(1.68 \pm .39) \times 10^2$	$(2.89 \pm .46) \times 10^2$	
^{235}U	$(1.42 \pm .02) \times 10^7$	$(1.47 \pm .02) \times 10^7$	$(1.48 \pm .22) \times 10^7$
^{234}U	$(4.38 \pm .06) \times 10^8$	$(4.40 \pm .50) \times 10^8$	
$^{212}\text{Pb}(^{232}\text{U})$	$(3.70 \pm .80) \times 10^4$	$(3.67 \pm .02) \times 10^4$	$(3.69 \pm .02) \times 10^4$
$^{233}\text{Pa}(^{237}\text{Np})$	$(7.80 \pm .35) \times 10^3$	$(7.78 \pm .43) \times 10^3$	$(7.70 \pm .44) \times 10^3$
^{231}Pa	$(8.19 \pm .19) \times 10^3$	$(6.68 \pm 1.37) \times 10^3$	
^{227}Ac (chain)	$(2.38 \pm .22) \times 10^3$	$(3.60 \pm .16) \times 10^3$	$(3.05 \pm .21) \times 10^3$
^{229}Th (chain)	$(1.76 \pm .15) \times 10^2$	$(1.32 \pm .55) \times 10^2$	$(1.46 \pm .61) \times 10^2$
^{226}Ra (chain)	$(3.23 \pm .12) \times 10^2$	$(3.15 \pm .24) \times 10^2$	$(3.73 \pm .47) \times 10^2$

counting data and the analytical data is quite good, proving that our understanding of the self-absorption correction is adequate for uniform samples. The amounts of $^{234\text{m}}\text{Pa}$ and $^{234\text{g}}\text{Pa}$ (^{238}U daughters) determined by gamma spec are too high, due, in part, to poor nuclear data, and, perhaps, an improper subtraction of natural uranium lines in the detector background. There is also a significant deviation between the amounts of ^{227}Ac determined from radiochemistry, and that determined from the measurement of its equilibrium decay products through their gamma rays. It is worth noting that both ^{232}U , through a 2615-keV gamma ray emitted by equilibrium ^{208}Tl , and ^{234}U , through a 0.04%-abundant 121-keV gamma ray, could be measured in the same gamma spectra. It is also worth noting that the concentration of ^{232}U returned by gamma spec is of much higher precision than that measured through alpha spec following chemical isolation; this is caused by the combination of the low background at high photon energies and the limitation on the amount of activity in a uranium sample before it becomes too thick to permit alpha spectroscopy. The ^{232}U content of a 3-gram sample of this material (assuming that the sample is old enough that 1.9-year ^{228}Th is in equilibrium) could be measured to $\pm 10\%$ precision with gamma spec in a counting interval of as little as two hours.

The age of the sample can be determined from gamma measurements of ^{235}U and ^{231}Pa (21.6 ± 4.7 years), from ^{235}U and ^{227}Ac (30.5 ± 0.9 years), and from ^{234}U and ^{226}Ra (17.8 ± 3.4 years). Both the $^{235}\text{U}/^{231}\text{Pa}$ and $^{234}\text{U}/^{226}\text{Ra}$ ages are consistent with the higher-precision values obtained through radiochemical analysis; however, the error bars are large enough that one would not realize that these nuclide pairs actually define different ages (see Table II). The $^{235}\text{U}/^{227}\text{Ac}$ age obtained from gamma spec is not compatible with that obtained through radiochemistry, and is somewhat nonsensical compared to the other ages in light of the chemical properties of the elements. The gamma spec measurements would lead one to conclude that the sample was last cleaned 19.1 ± 2.8 years prior to the analysis time (compared to 19.35 ± 0.41 years from radiochemistry), and was contaminated with ^{227}Ac (wrong) and 1500 ± 90 ppb ^{237}Np (compared to 1570 ± 70 ppb from radchem) at some later time. The plutonium and americium contaminants were invisible to gamma spec. Once the age has been determined, the ^{229}Th concentration can be used to calculate that the content of the signature nuclide ^{233}U was $(0.87 \pm 0.28) \times 10^{15}$ atoms/ml (compared to $(1.14 \pm 0.08) \times 10^{15}$ atoms/ml from radchem), completing the suite of uranium isotopics (except for ^{236}U).

Tables V and VI compare the gamma counts of strong and weak solution standards, respectively, with the scaled analytical data.

TABLE V. COMPARISON OF ANALYTICAL DATA WITH COUNTS OF THE STRONG LIQUID STANDARD.

<u>NUCLIDE</u>	<u>DPM, SCALED ANALYTICAL</u>	<u>DPM, GAMMA SPEC</u>
$^{234m}\text{Pa}(^{238}\text{U})$	$(7.73 \pm .09) \times 10^4$	$(12.2 \pm 1.8) \times 10^4$
$^{234g}\text{Pa}(^{238}\text{U})$	$(1.00 \pm .23) \times 10^2$	$(1.98 \pm .39) \times 10^2$
^{235}U	$(8.49 \pm .09) \times 10^6$	$(9.22 \pm .12) \times 10^6$
^{234}U	$(2.62 \pm .04) \times 10^8$	$(2.45 \pm .18) \times 10^8$
$^{212}\text{Pb}(^{232}\text{U})$	$(2.22 \pm .48) \times 10^4$	$(2.20 \pm .02) \times 10^4$
$^{233}\text{Pa}(^{237}\text{Np})$	$(4.67 \pm .21) \times 10^3$	$(5.05 \pm .31) \times 10^3$
$^{227}\text{Ac}(\text{chain})$	$(1.42 \pm .13) \times 10^3$	$(1.65 \pm .14) \times 10^3$
$^{229}\text{Th}(\text{chain})$	$(1.05 \pm .09) \times 10^2$	$(1.54 \pm .44) \times 10^2$
$^{226}\text{Ra}(\text{chain})$	$(1.94 \pm .08) \times 10^2$	$(3.60 \pm .44) \times 10^2$

TABLE VI. COMPARISON OF ANALYTICAL DATA WITH COUNTS OF THE WEAK LIQUID STANDARD.

<u>NUCLIDE</u>	<u>DPM, SCALED ANALYTICAL</u>	<u>DPM, GAMMA SPEC</u>
$^{234m}\text{Pa}(^{238}\text{U})$	$(2.58 \pm .03) \times 10^4$	$(3.94 \pm .57) \times 10^4$
$^{234g}\text{Pa}(^{238}\text{U})$	$(3.35 \pm .77) \times 10^1$	$(9.80 \pm 4.40) \times 10^1$
^{235}U	$(2.83 \pm .03) \times 10^6$	$(2.90 \pm .04) \times 10^6$
^{234}U	$(8.75 \pm .12) \times 10^7$	$(7.20 \pm .70) \times 10^7$
$^{212}\text{Pb}(^{232}\text{U})$	$(7.39 \pm 1.60) \times 10^3$	$(7.35 \pm .08) \times 10^3$
$^{233}\text{Pa}(^{237}\text{Np})$	$(1.56 \pm .07) \times 10^3$	$(1.71 \pm .11) \times 10^3$
$^{227}\text{Ac}(\text{chain})$	$(4.75 \pm .43) \times 10^2$	$(4.96 \pm .52) \times 10^2$
$^{226}\text{Ra}(\text{chain})$	$(6.46 \pm .25) \times 10^1$	$(5.80 \pm 1.60) \times 10^1$

The conclusions one would draw from gamma-ray counts of the solution standards are similar to those from counting the metal foil. Again, the values of ^{238}U and ^{227}Ac determined from gamma spec were significantly higher than those obtained from radiochemistry. In general, the results of the gamma counts of the solution standards are of lower quality than those of the metal counts, both because of the smaller sample sizes and because of the use of Cd and Pb absorbers on long counts. These absorbers were used to improve the quality of the high-energy region of the gamma-ray spectra by reducing the total photon rate, permitting a smaller detector-sample distance; however, the improvement in the determination of ^{232}U was negligible, while the loss of information at low energies was substantial.

V. CONCLUSIONS

On the basis of this work, the non-destructive analysis of HEU through gamma-ray counting is of limited value. With an old sample, it was possible to measure ingrown daughter activities whose concentrations defined both the age of the sample and the minor uranium isotopes (^{232}U , ^{233}U , and ^{234}U); however, (except for the ^{232}U concentration) this information was of significantly lower quality than that returned by the radiochemical analysis. Real forensic samples of HEU are likely to be considerably less than 20 years old, so gamma-ray intensities of these ingrown daughters will be much lower relative to those from ^{235}U (+ ^{231}Th) decays, and consequently much harder to observe. Other than the ^{237}Np concentration, gamma spec did not return values for any of the contaminant nuclides.

The two solution standards are stored in the B-151 counting facility. Anyone who wishes to try to improve the non-destructive technique (e.g. via Compton suppression?) is welcome to use these samples, though they must remain in B-151.

The radiochemical analysis gave a detailed time line for the production of the material: The uranium was mass-separated prior to 1967 in a plant in which reactor-irradiated uranium had been used as feed. It was purified for the final time in 1974, using a chemical procedure that did not completely remove protactinium. When the material was converted to metal and rolled into foil, it was contaminated with weapons-grade plutonium (last cleaned of americium in 1969) and neptunium (containing ^{238}Pu). This trace-element analysis suggests that the sample was prepared in a plant that had both military (w.g. Pu) and non-military (^{237}Np) clients in the '60's, and was involved in re-using old HEU parts; sort of like Oak Ridge. The ^{237}Np contamination in the original sample is so substantial that one might also draw the alternative conclusion that it might have been added on purpose as a tracer of some kind.

If we are going to get into the business of analyzing HEU samples there are several items that need to be improved on:

1. Half-life of ^{234}U . Since ^{234}U is by far the most intense alpha activity in an HEU sample, an error in its half-life directly translates itself into a systematic error on all the activities in the sample ($A = \ln 2 / t_{1/2} * N$). The error bar on the literature value (At.Data Nucl.Data Tables 40, 523 (1983)) of the ^{234}U half-life is 1%, far worse than the errors on any of the other long-lived uranium isotopes.
2. Determination of ^{233}U with TIMS. The value for ^{233}U given in Table 1 was determined from the relative amounts of ^{230}Th and ^{229}Th in the thorium chemical fraction and the age extracted from the ^{234}U decay chain. At present, our mass spec

capability has insufficient dynamic range to be able to return a value for such a minor component of the HEU. This precludes using the $^{233}\text{U}/^{229}\text{Th}$ pair for age dating. The Th analysis is very time consuming and not terribly accurate, and ^{233}U is an important "signature" nuclide, so a mass-spec capability should be developed.

3. Absolute intensities of the gamma rays from ^{231}Th and ^{231}Pa decays. The error bar on the ^{231}Th intensity set is $\pm 10\%$, and that for ^{231}Pa is $\pm 20\%$. The ^{231}Pa set is particularly bad because the relative intensities aren't right either. It would be easy to determine either of these sets to an accuracy of $\pm 5\%$, and with a little effort we could do much better than that.

4. Improvements to the chemistry. It would simplify the data reduction to generate Am, Ac, and Ra fractions which are not contaminated with one another (see appendix). This requires some work on the last cation-exchange step. It should also be possible to pull a Pb fraction off this column, which would provide another means of dating the sample ($^{226}\text{Ra}/^{210}\text{Pb}$ pair).

5. Different alpha-counting technique for samples with Rn daughters. Calculation of the 2-pi detector efficiency is difficult when some of the daughter decays occur in the sample, some in the counting gas, and some completely outside the detector. It was done by measuring the apparent half life and initial activities of ^{220}Rn following a short count of each sample. Apparent detector efficiency is different for each sample, determined by sample thickness. We should probably develop a liquid-scintillation method for these kinds of samples.

6. The literature values for the relative intensities of the gamma rays emitted in the decay of ^{235}U with energies in excess of 265 keV do not match the counting data from this measurement, often by as much as an order of magnitude. It is not clear whether the problem is in the nuclear data, or in the way GAMANAL treats very small peaks on top of a large background. The intensities of higher-energy photons are least affected by source non-uniformity, and it is important to be able to interpret them.

7. Identification of gamma-ray doublets for age dating. We can search for pairs of gamma rays emitted at similar energies, so that relative absorption losses will be a calculable small correction for irregularly-shaped or non-uniform samples; this is a technique developed for defining the isotopes of plutonium. Pairs of gamma rays that have the potential of being useful in age dating HEU are (1) at 267.6 keV (^{235}U) and 269.6 keV (^{227}Ac), and (2) at 282.9 keV (^{235}U) and 283.6 keV (^{231}Pa). Unfortunately, this technique requires extensive calibration since the relevant nuclear data is less than adequate.

8. Surface study by Secondary Ionization Mass Spectroscopy (SIMS). While the age of the plutonium present in the sample required that contamination occurred after chemical processing, it was impossible to determine the metallurgical step responsible. If Pu and Np were introduced into the sample during rolling (as seems likely), it would be concentrated near the surface of the material. A depth-profiling technique such as SIMS should be developed to resolve this effect. In a complete analysis, a SIMS procedure could be performed between a gamma-spec measurement (for ^{232}U) and the destructive radiochemical analysis.

VI. ACKNOWLEDGMENTS

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APPENDIX: PROCEDURE FOR THE RADIOCHEMICAL ANALYSIS OF A NITRIC ACID SOLUTION OF HEU.

Aliquots of the Orallo stock solution (HNO_3) of 0.050 ml each were diluted to 10 ml in volumetric flasks with 8M HNO_3 . Each flask was mixed thoroughly and allowed to sit overnight. Three counting samples were prepared from each dilution by quantitatively stippling 0.050-ml aliquots on 1"-diameter platinum disks. The nine samples were counted in calibrated 2-pi gas-proportional counters to determine the absolute alpha disintegration rate of a given volume of the Orallo stock solution.

Four samples were prepared for analytical chemistry as follows: One sample was prepared from 0.499 ml of the Orallo stock solution, spiked with standard aliquots of ^{236}Pu and ^{243}Am tracers. A second sample was prepared from 0.499 ml of the Orallo stock solution, spiked with an aliquot of ^{237}Np tracer. A third sample contained approximately 0.75 ml of the Orallo stock solution without any added tracer activities. A fourth solution contained aliquots of ^{236}Pu , ^{243}Am , and ^{237}Np , without any Orallo stock solution. The samples were processed simultaneously; the combination of spiked, unspiked, and spike-only samples provides a means of checking for cross contamination and determining chemical yields.

Each analytical sample was evaporated to a moist deposit, 9M HCl was added, and the samples were again evaporated. The samples were dissolved in 1.5 ml 9M HCl and 1 drop 8M HNO_3 , and were heated gently for about an hour. Each sample was loaded on an 8-mm dia by 15-cm long Dowex 1x8 anion-exchange column, which was washed with 10 ml 9M HCl . The load and wash solutions contained Th, Ac, Ra, and the transplutonium elements. Pu was then eluted from the columns with 10 ml of a warm solution consisting of 1 part con HI to 15 parts 10M HCl , followed by 10 ml 9M HCl . Np and Pa were then eluted from the columns with 15 ml of a solution that was 4M in HCl and 0.1M in HF . U was then stripped from the columns with 0.5M HCl . All the eluent fractions were evaporated to dryness.

Dry Pu fractions were dissolved in warm 8M HNO_3 containing a partial drop of sat'd NH_4NO_2 and were loaded onto 4-mm dia Dowex 1x8 columns. The columns were washed with 8M HNO_3 , then with 9M HCl ; Pu was then eluted with HI/ HCl as before.

The dry Np/Pa fractions were dissolved in warm 8M HNO_3 containing a partial drop of sat'd NH_4NO_2 and were loaded onto 4-mm dia Dowex 1x8 columns. The columns were washed with 8M HNO_3 , then with 9M HCl . Pa was then eluted with a solution which was 9M in HCl and 0.02M in HF . Np was then eluted with a solution which was 4M in HCl and 0.1M in HF . Pa and Np samples were evaporated to dryness. Pa fractions were then dissolved in 9M HCl and loaded onto 2.5-mm dia Dowex 1x8 columns. The columns were washed with HI/ HCl , then Pa was eluted with 9M HCl /0.02M HF . Np fractions were dissolved in 9M HCl and loaded onto 4-mm dia Dowex 1x8 columns. The

columns were washed with 9M HCl, then with 9M HCl/0.02M HF. Np was eluted with 4M HCl/0.1M HF. To provide extra decontamination from ^{234}U , Np fractions were evaporated to dryness, dissolved in 9M HCl, and loaded onto 2.5-mm dia Dowex 1x8 anion columns. The columns were washed with 9M HCl, then Np was eluted with 4M HCl/0.1M HF.

The samples containing Th, Ac, Ra, and the transplutonium elements were dissolved in 8M HNO_3 containing a partial drop of sat'd NH_4NO_2 . These solutions were loaded warm onto 4-mm dia Dowex 1x8 columns. The columns were washed with 5 ml 8M HNO_3 ; load and wash solutions contained Ac, Ra, and the transplutonium elements. Th was eluted with 9M HCl. The Th samples were evaporated to dryness, dissolved in 8M HNO_3 and loaded onto 2.5-mm dia Dowex 1x8 columns. After copious 8M HNO_3 washes, Th was eluted from the columns with 9M HCl.

Fractions containing Ac, Ra, and the transplutonium elements were evaporated to dryness, dissolved in water, and loaded onto fully-conditioned 4-mm dia Dowex 50x4 cation-exchange columns. The columns were washed with water, with 0.5M HCl, and with 1.0M HCl. The columns were also washed with 2M HCl into glass planchets, which were dried and surveyed for alpha activity. The 2M HCl wash continued until a marked increase in gross alpha activity was observed over the steady-state Pb/Po daughter activities. Am/Ra fractions were eluted with 4M HCl, then Ac/Ra fractions were eluted with 9M HCl.

All final column eluents (except U fractions) were evaporated to dryness, transferred to tungsten filaments using 6M HCl, and flashed onto 1"-dia Pt disks by sudden heating of the filaments. Several small aliquots of the dilutions of the stock solution were similarly prepared. Np, Pa, and Th samples were mounted in plastic gamma-spec holders and gamma-counted for ^{239}Np , ^{233}Pa , and ^{231}Th chemical yield indicators, respectively. These samples were then dismounted and counted for gross alpha activity as a function of time using calibrated 2-pi gas-proportional counters. All samples were pulse-height counted for alphas with surface-barrier detectors. Following the counting measurements, the unspiked Pu fraction was dissolved off its Pt disk with aqua regia, evaporated to dryness, dissolved in 9M HCl and loaded onto a 2.5-mm dia Dowex 1x8 column. After washing with 9M HCl, Pu was eluted with 0.5M HCl. This solution was evaporated to a small volume and submitted for mass spectrometric analysis. Mass spec was also performed on small aliquots of dilutions of two of the dilutions of the stock Orallo solution and on a small aliquot of the U chemical fraction from the unspiked sample.

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